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AD-A266 495

NAVSO P 3678

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ESN INFORMATION BULLETIN

This publication is an official publication of the Office of Naval Research European Office. It describes research that is being conducted in Europe and the Middle East.

Commanding Officer . . . . CAPT John M. Evans, USN
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93-04

In This Issue. . .

SPECIAL FOCUS—MATERIALS

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OCEANOGRAPHY

High-Temperature Structural Materials for Aerospace: The Situation in the United Kingdom

by Anthony G. Evans, a visiting scientist at the Office of Naval Research European Office, while on leave from the University of California, Materials Department, Santa Barbara, California.

KEYWORDS: composite materials, Ti alloys, process modeling, aerospace, simulation

SUMMARY

Activities in the United Kingdom concerned with high-temperature structural materials for aerospace provide some interesting contrasts with those in the U.S. On the positive side, major investments have been made in advanced processing facilities at several academic centers, particularly at Oxford and Birmingham Universities. These have been paid for by the Science and Engineering Research Council (SERC). There is also a strong effort in process modelling and simulation, with software deliverables. In this area, funding originates both with industry and the SERC. One reason for this emphasis on integrated processing research is the more open dialogue between industry and academia in advanced processing technology. I suspect that this occurs because sponsored research at universities can be subject to confidentiality agreements. With this arrangement, the sponsor has the right to delay publication of the research and can have first refusal on patent applications.

There are obvious problems with this, especially with regard to Ph.D. research. However, imaginative compromises have been found whereby the Ph.D. research is in the public domain and the postdoctoral research, etc., is subject to confidentiality. Some trust is clearly involved, based on past working relationships. I believe that the U.S. can learn from this approach in order to improve the scope, the quality, and the integration of processing research on structural materials. Although in some ways the concept is the same as that used for Intelligent Processing of Materials (IPM) programs in the U.S., more effective use appears to be made of the talent and capabilities available at academic institutions.

On the negative side, there is negligible integration of effort on the properties-to-design activities. There is a surprising lack of interaction between materials and applied mechanics (even though good people in both areas may exist at the same university). The exception is the program in the Engineering Department at Cambridge. There is also limited dialogue between the microstructure groups (electron microscopy), the processing groups and those measuring properties. The situation is similar to that in the U.S. about 10 years ago, but with no obvious signs that the situation will improve. Some individuals are trying to do all of these things, with sporadic success. But the efforts cannot be sustained with a good balance of activities.

Relationships between industry and academia indicate long-term problems. In particular, the relationships between Rolls-Royce and academia are a frequent topic of discussion. While I found the Rolls technical staff to be very helpful and ready of discuss topics of mutual interest, the consensus appears to be that Rolls is not decisive about the role of advanced materials in the company. At this stage, their strategy appears to be one of keeping a finger in the pie. They have some in-house effort on Ti (titanium) MMCs (metal matrix composites) and on CMCs (ceramic matrix composites). They also sponsor (jointly with the government) academic programs on these materials. However, the lack of a definitive, applications-driven program causes the research to be unfocused. British Aerospace also sponsors activity in the field, but they appear to be more focused on PMCs and have little effort on MMCs and CMCs. Furthermore, the advanced materials sector of U.K. industry appears to be withdrawing. At this stage, there does not seem to be any industrial producer of either CMCs or Ti MMCs. Additionally, there are no ceramic fiber producers in the U.K.

It appears to me that the long-term viability of advanced structural materials in the U.K. is in jeopardy. This situation may be used to advantage

by the U.S. community, by attempting to involve the real centers of excellence in the U.K. in U.S.-directed research.

One mechanism for exploring opportunities of this type is to hold small topical study groups that include U.S. and U.K. scientists. The objective would be to decide on multi-investigator activities in the area of advanced structural materials that could benefit from the combined expertise available in both countries. This has been done previously, leading to the successful involvement of the Ashby group at Cambridge. An obvious opportunity exists in the area of processing and process modelling.

During my visits to programs in the U.K. that were concerned with high-temperature structural materials for aerospace, I had the opportunity to critique the overall effort. As a result of these visits, plus literature and technical articles, this report summarizes high points of the U.K. program. Numerous locations and research activities are not mentioned. The implication is that these other efforts are not novel and do not contribute in a special way to the international research situation on these materials.

The scope of my investigation was confined primarily to composite materials, especially metal, ceramic, and intermetallic matrix composites. It did not attempt to include polymer matrix composites. Highlights include the following three major areas:

- the Interdisciplinary Research Center on Materials for High-Performance Applications,
- programs on design at Cambridge and Oxford Universities, and
- the Rolls Royce Advanced Ceramic Composites Center.

In addition to these three, a few smaller efforts were notable. These have been grouped together in the final section of this report.

INTERDISCIPLINARY RESEARCH CENTER ON MATERIALS FOR HIGH-PERFORMANCE APPLICATIONS

The U.K. Science and Engineering Research Council (SERC) (which is the U.K. equivalent to our National Science Foundation) has funded a 6-year, $24M Interdisciplinary Research Center (IRC) program jointly at the Universities of Swansea and Birmingham, U.K., sponsored by Rolls Royce. The materials being investigated are for the U.K. aerospace industry, with primary emphasis on Ti alloys, intermetallics, ceramics, and their composites. The objective is to relate manufacturing to composite performance. The program has indefinite duration, provided that each 3-year review proceeds satisfactorily, and is now beginning its fourth year.

The ideas behind this IRC evolved after Rolls Royce visited the Defense Advanced Research Agency's University Research Initiative program on High-Performance Composites in 1987. About 60 percent of the effort is at Birmingham, where they are concentrating on processing and basic physical metallurgy issues. Research includes growing single-crystal fibers, developing tape casting, and slurry processing. The remaining 40 percent effort is at Swansea. Research here is in two related parts:

- developing software to facilitate forging and consolidation as well as design; and
- acquiring the creep and fatigue data needed to devise constitutive laws, based on continuum damage mechanics.

I judge this effort as follows:

Equipment

Considerable funding has been provided for equipment—about $14 million thus far, with new funds each year. This has been used to set up first-class facilities for testing, processing, and characterization.

Testing

Between those at Birmingham and at Swansea, the combined testing facilities have about five times more capacity than any academic program in the U.S., especially for fatigue and creep testing of composites. The machines also have good extensometry, plus optical/laser probes. Paul Bowen at Birmingham and Brian Wilshire at Swansea are the orchestrators.

The Swansea group has an outstanding capability for creep and fatigue testing, particularly under multiaxial loads. They have more than 20 relatively new servohydraulic machines with temperature capability up to 1600°C, plus good extensometry. In addition, they have more than 30 constant stress creep machines and two Gleeble simulators. More than $6M has been invested in the facility, which is available to U.S. programs, with proprietary work being negotiable. I believe that we would benefit by initiating a creep testing effort on MMCs (metal matrix composites) and CMCs (ceramic matrix composites) at Swansea that ties into model development programs in the U.S.

Processing

The processing facilities are on an industrial scale, but as yet they are not comprehensive. Birmingham has a 150 kW torch plasma system (costing $1.6M) being used for Ti alloys and Ti aluminides. They make large billets and also spray-form tubes. The material quality is good; the billet material can be purchased if anyone is interested!

They have also invested heavily in a laser system for growing single-crystal oxide fibers. However, they have neither the expertise nor the monitoring/control system needed to produce significant quantities of good-quality fibers in the foreseeable future. I suspect that this effort may go under.

The other processing facilities are typical—although new and of good quality. They include HIPs (hot isostatic pressing), a large squeeze caster, and a facility for gas pressure superplastic forming.

Characterization

As in most other U.K. universities, Birmingham has lots of transmission electron microscopes (TEMs) and scanning electron microscopes (SEMs) with all the bells and whistles. In addition, they have a SEM dedicated to in situ fatigue crack growth measurements, with a hot stage. The latter is a real asset.

Research

General

At this stage, the IRC's research progress is fragmentary. They have conducted some very good testing and characterization, especially on Ti MMCs. The material is from Textron, purchased by Rolls Royce, and provided gratis to the University. TEM characterization of intermetallic microstructures is also a strong effort. However, work on CMCs is disappointing.

In general, they have not yet been able to make any composites of a quality suitable for testing and are concerned about their ability to succeed with this objective, i.e., connecting processing to properties. They have not succeeded in involving the applied mechanics community in the U.K. Hence, their micromechanics and design efforts are weak.

Highlights

The fatigue work on Textron Ti MMCs is comprehensive, including some nice in situ observations of crack growth in the SEM and fiber push-out information. However, their lack of expertise in applied mechanics limits their overall ability to move forward quickly. Nevertheless, the people are good (Paul Bowen and John Knott), and I expect this group to continue conducting international quality research in this area. We should think of ways to use their facility and testing expertise to assist efforts in the U.S.

One interesting idea on CMC processing is being pursued by Peter Marquis (apparently, the idea originated at Rolls). They are using an electrophoretic procedure to infiltrate fiber preforms with submicron ceramic powders. This procedure

allows them to achieve remarkably high green density in the matrix. They claim up to 80 percent, although this seems higher than theoretically possible (unless they are using a bimodal powder: they did not admit to this). Following infiltration, they are strengthening without shrinkage, by heat treating in the surface diffusion temperature range (Fred Lange's original idea).

At Swansea, I was shown a program that simulates forging and found it to be user-friendly and comprehensive. It displays deformations, stresses, temperatures, grain sizes, and interdiffusion profiles. I believe that it is widely used for right-first-time forging practice in several industrial sectors. The Swansea group, led by Prof. Russell Evans, has some unique capabilities, put into place through IRC funding. Most relevant to U.S. interests, I believe, is their group of software experts who incorporate user-friendly aspects into finite-element programs. Even I could use their programs. The academic programs in the U.S., in my experience, have not emphasized this capability.

I explored the possibilities of using the Swansea group to develop software programs suitable for design and lifing with continuous fiber MMCs and CMCs. They are willing and able to do this. A key aspect here is that, unlike U.S. universities, all of the U.K. universities can do proprietary research, with intellectual property rights being negotiable during contract discussions. I strongly recommend that this possibility be investigated, particularly with regard to creep and fatigue lifing. The models would be provided by the U.S. investigators and the software developed at Swansea.

Future Prospects

This IRC will become a major center for research on aerospace materials. The SERC investment in facilities, which continues unabated, will ensure this.

Their major problem is a lack of fibers in the U.K., with associated fiber-coating technology. Consequently, they may never be able to make good-quality composites. The exception may be CMCs, using the electrophoretic method, with fibers provided by the Japanese. Nevertheless, since Rolls Royce acquires materials in the U.S., which they provide to the IRC, the testing and analysis efforts can be expected to proceed rapidly.

DESIGN ACTIVITIES

SERC Design Center at Cambridge

Two years ago a collaborative team was formed at Cambridge University to create the Design Center within the Engineering Department. The participants are from Materials Engineering, Computer Engineering, and Mechanical Engineering. Mike Ashby is the Materials participant. The overall objective is to conduct:

- Concept Modeling,
- Functional Modeling, and
- Materials Selection.

The effort on Materials Selection in Design is well advanced. The group has created a computer-aided design (CAD) software package that incorporates a comprehensive database and, more importantly, performs sophisticated materials selection functions. To accomplish this, the group has hired a well-paid computer programmer who is capable of generating robust software. I used the program and was impressed by its simplicity and the level of decision-making that could be accomplished in real time. In particular, a much higher level of rapid decision making becomes feasible when using this software program than when using the graphs and maps that appear in the written reports. It is possible to simultaneously impose a set of merit indices/design parameters and select materials that fit within a design window. This is accomplished without preconceived biases that the preferred materials might be metallic, polymeric, ceramic or composites, or even natural (wood, etc.).

The software, referred to as the Cambridge Materials Sector, is available for purchase. I believe that it will be particularly useful for teaching purposes in Design and Materials. It will also help Materials Producers who wish to assess their menu of (existing and new) materials against materials in the database for various possible applications: structural, functional, thermal, etc. It could be useful for Materials Research, as a tool for

deciding on worthwhile research directions in materials development programs. That is, to decide whether a newly proposed material really has advantages over already available materials and, if so, how much. I believe that if this software had been generally available, several large materials research efforts within the last decade would not have been initiated.

Presently, the software includes information on elastic and thermal properties, yield strength, tensile strength, density, toughness, and cost per pound. Further development underway will add fatigue and creep modules within the next year. Beyond that, there are plans to consider thermal fatigue.

One deficiency with the present system is that the database, although extensive, contains only commercially available materials. If an arrangement could be found that coupled MMC and CMC databases that exist in the U.S., the program would have even wider applicability. Ashby is willing to discuss approaches for achieving this. Contact either myself or Ashby if you have any interest.

The Design Program at Oxford

An impressive testing and analysis facility has been developed by Prof. Carlos Ruiz at Oxford. This facility has been funded continuously by Rolls Royce, at about $1M per year, for more than 7 years. It includes all of the usual dynamic facilities for compression, tension (split Hopkinson bar), and tension/torsion testing, plus an impressive Moiré interferometer (with excellent software) for experimental measurement of deformations. The group also uses the ABAQUS code when calculations are required. Because the work is funded by Rolls, most of the "good stuff" does not appear in the open literature. This group has broad experience in metals and ceramics, as well as in polymers and ceramic matrix composites. Their particular expertise seems to be on delamination damage in composites and on fretting fatigue (in everything). For the former, they have adopted C-specimens and have just completed a comprehensive analysis of that specimen. They also use Iosipescu specimens for shear measurements and have done an error assessment for that specimen. I have reports on both.

The group has developed an interesting apparatus for studying fretting fatigue in ceramics as function of temperature. They have completed a study concerned with contacts between silicon nitride and superalloys and found degradation effects caused by silicide formation. Rolls has stopped sponsorship of this work, but Ruiz is keen to continue. Any offers? I have their paper on this subject.

My assessment of this effort is that it is well-equipped and efficiently uses combinations of experiment, back-of-the-envelope, and finite-element calculations to solve a diverse range of problems in engine materials. A good example has been their design against impact of Ti alloy honeycomb panels to be used for fan blades.

Compressive Failure of Composites

A program at Cambridge headed by Norman Fleck, who collaborates with Bernie Budiansky, has made considerable progress in both understanding and characterizing the compressive failure of composites. In particular, they have devised a mechanics methodology for predicting effects of holes and notches on compression strength, based on efficient use of laboratory tests. The mechanics is analogous to the large-scale bridging mechanics developed for tensile failure of composites. The procedure should be applicable to both polymer and metal matrix composites.

They have a testing capability that has been used (almost exclusively) for polymer matrix materials to validate the methodology. They are prepared to repeat the process for Al and Ti MMCs if the material can be provided. Any offers?

The test and analysis capability has recently been extended to include creep, which might be particularly relevant to MMCs.

The ability to explicitly relate compressive strength to constituent properties (matrix, interfaces, fibers) is not yet completed. Much of the mechanics has been done. Data on MMCs would be particularly useful for bringing this to fruition.

ROLLS ROYCE ADVANCED CERAMIC COMPOSITES CENTER

For several years, Rolls has centered their CMC development at a site on the University of

Warwick; they are located next door to the Physics Department (of which Michael Lewis is the senior faculty member). Now, all of their composites effort is about to be consolidated at Derby. Consequently, the Warwick laboratories, as well as laboratories at Bristol, are expected to be moved to Derby soon.

During this visit, I felt that the Rolls group (led by Andrew Bennett) and the Warwick University group (Michael Lewis) were unexpectedly open with me about their strategy and their materials efforts. (Note: Lewis does research under confidentiality agreements with Rolls, which is typical of other university efforts in the U.K., and the results have not appeared in the open literature. Consequently, the extent of this effort surprised me.)

The basic Rolls strategy on CMCs is to have enough internal effort on processing, testing, and design to be "intelligent customers" when they purchase materials and components from suppliers. They can produce glass ceramic and silicon nitride matrix systems by hot pressing and superplastic forming and have generated components with surprisingly complex geometry. They use Japanese fibers for the glass ceramic matrices and Textron fibers for silicon nitride. They also have a chemical vapor impregnation (CVI) system for producing SiC/SiC.

They have acquired a variety of CMCs for testing and analysis including SiC/CAS, SiC/SiC (CVI), SiC/Al_2O_3 (Lanxide).

On the design side, they have adopted an interesting strategy that seems to have put them in a strong position. They have produced a model composite consisting of a polymer fiber in a brittle polymer matrix that, when tested, has the same generic features as CMCs. Namely, it exhibits matrix microcracking, with interface sliding, and has the same modulus ratio (fiber-to-matrix) as typical CMCs. They produce test coupons and subelements from this material, using a variety of 2-D and 3-D woven and knitted fiber architectures. They then test the subelements and develop relationships between coupon tests and subelement performance. Based on these test results, they are also working on nonlinear subroutines for finite-element codes. This approach seems to have brought them up the learning curve quickly, especially for such subelements as T-junctions and pin-loaded holes.

At this stage, they do not appear to be as aware of fiber coating issues as do their counterparts in the U.S. Also, the lack of fiber manufacturers in the U.K. is a serious concern, given the demise of the ICI effort and the Sigma fiber.

I had a brief discussion about Ti MMCs but did not meet the key people from Derby; a return visit is needed. I found out (although it is probably well known) that there is a major European effort on a ring rotor made from Ti MMCs.

ADDITIONAL HIGHLIGHTS

Materials Processing at Oxford

Perhaps the most unexpected feature of my visit to Oxford was the time (too short) spent in the new Materials Processing Facility. This facility, which is nearly complete, has been developed by Prof. Brian Cantor. The facility includes a fully automated Plasma Spray Unit, with all the bells and whistles, paid for by SERC, plus an Osprey-type atomizer and spray unit, plus a squeeze casting system, each with lots of sensors and controls. As I have been finding elsewhere in the U.K., much of the actual research is funded by a joint industry/government program and is subject to confidentiality agreements. The work on their spray forming unit has been on Al alloys and has been sponsored by Alcan. However, they are about to begin a program on Ni alloys, sponsored by Rolls Royce. The plasma spray unit will be used primarily for Ti alloys, including aluminides and their composites. I was given the impression that they are looking for research sponsorship in this area and are open to the discussion of possibilities.

My understanding is that their modus operandi at Oxford is as a basic arm of Industrial programs. A particular emphasis has been on sensing and modeling particle size distribution effects on solidification (plus remelting), as well as the trajectories of particles impinging onto an insulated surface. The objective has been to create an active surface that has the correct solid/liquid mix such that the solids act as nuclei for final solidification and provide a fine-scale, homogeneous microstructure.

The modeling effort has also addressed overall control of the billet geometry to minimize material removal needed prior to extrusion.

For their new effort on plasma spray, the Ti alloy powders will be provided by the Birmingham IRC and the fibers will be Sigma, with TiB_2 coatings. It appears to me that we should "adopt" this facility and arrange for Oxford to do some basic modelling, plus provide Ti MMC ta;e, for our research efforts in the U.S.

Ceramic Composites at Warwick

Warwick University has an impressive effort in several areas. They process CMCs by hot pressing tapes and evaluate basic properties, such as the interface sliding, tensile stress/strain curves, and creep rates, and conduct TEM characterization. Variables they have looked at comprehensively include the effects of expansion mismatch and coating thickness. In particular, they have related the sliding stress τ to the coating microstructure, thickness, etc., and, in turn, connected τ to tensile strength and matrix cracking. To evaluate τ, Lewis has developed a unique fiber push-through system for testing small-diameter fibers in the SEM, which operates at high stress levels and obviates some of the limitations found when using the nanoindentor. It uses a piezoelectric load cell and a capacitance transducer, with flat-ended diamond indentors produced in their laser facility at Warwick. The apparatus fits within the SEM, which is used to monitor the top face displacements and provide video images.

Ceramic Composites at Bath

At Bath, they produce a low-cost CMC with complex shape capability by using a processing approach analogous to resin transfer molding (RTM). For matrix infiltration into the fiber preform, they use an oxide gel with an appreciable solids content, followed by freeze drying. They claim that the ice crystals that form upon drying do so without significant volume change. Consequently, upon warming, the melting of the ice leaves a durable structure with relatively large diameter and homogeneously dispersed void channels. This structure can be sequentially infiltrated and sintered without disruption to form the final (porous) product, with a seemingly homogeneous matrix microstructure.

The advantages that I perceive are the compatibility of the processing with existing RTM technology for polymer composites and the robust nature of this manufacturing route. Furthermore, the process has not been patented.

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Piezoelectric Materials Research in Europe

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KEYWORDS: piezoelectric; polycrystalline; poling; Curie Point; magnetics

INTRODUCTION

The Office of Naval Research (ONR) and Office of Naval Research European Office (ONR Europe) recently sponsored an international workshop on advances in piezoelectric materials and current research thrusts in Europe. "Perspectives on Piezoelectric Materials Research" was held at Elvetham Hall, near Basingstoke, England, 21-24 February 1993. The 27 invited delegates were drawn from industry, academia, and government research organizations in nine countries [Denmark, France, Federal Republic of Germany (FRG), Italy, Slovenia, Spain, Switzerland, the United Kingdom (U.K.), and the United States (U.S.)].

Several critical, interrelated issues were identified:

- variability of material properties,
- suitability of current Finite-Element Methods, and
- manufacturing methods and costs.

These are also major issues in the U.S. and are discussed in more detail below.

BACKGROUND

Piezoelectric materials both deform when a voltage is applied and produce a voltage when forcibly deformed. The deformation and voltage are proportional. This effect was first noted in certain single crystals by Jacques and Pierre Curie more than 100 years ago and occurs when there is an inherent polarity in the crystal structure. That is, unequal electron distribution in the smallest repeating crystalline unit cell creates a net electric dipole moment. Polycrystalline materials (for example, ceramics) do not normally exhibit piezoelectric activity, since the random orientation of their various crystal domains cancels out the individual electric dipole moments. However, by the mid-1940s it had been discovered that these individual crystal domains, and hence their dipoles, could be aligned by applying a strong electric field at elevated temperature. This process is called "poling" and is directly analogous to permanently magnetizing an iron nail by applying an external magnetic field. In fact, the parallels between magnetics and piezoelectrics are quite strong, and even the same terms (e.g., "Curie Point", "hysteresis", "ferroelectricity" vs "ferromagnetism") are used to describe similar phenomena.

Current piezoelectric materials research centers on three broad classes of materials: piezoceramics, piezopolymers, and piezocomposites (e.g., a piezoactive material embedded in a passive matrix).

Piezoelectric materials are most commonly used to both produce and detect vibrational energy. They form the heart of most sonar transducers, hydrophones, and projectors. Virtually all ultrasonic transducers and medical "ultrasound" equipment use them, often at frequencies of many megahertz. Also, piezoelectrics show great potential for use as both sensors and actuators in active noise and vibration control systems as well as other "smart" materials and structures.

Recent piezoelectric applications include piezoelectric motors, solid-state gyroscopes, and surface acoustic wave (SAW) chemical sensors. Intriguing recent biomedical research has shown that some piezopolymers by themselves, without any external electric circuitry, may stimulate severed nerves to reconnect.

PIEZOCERAMICS

A critical issue identified for piezoceramics lies in the variability of material parameters for a single nominal material. This was highlighted by both the producers and users. Many insights but no clear resolution emerged from extensive discussions. For example, in the classic lead zirconate-titanate (PZT) solid solution, the interesting material properties arise from compositions near the morphotropic phase—that is, the composition lying on the border between material having a rhombohedral lattice structure (zirconate side) and material having a tetragonal structure (titanate side).

Conceptually, a point boundary may exist in a single crystal. In practical ceramics, however, a boundary region of finite extent exists. Over this region, both the rhombohedral and tetragonal phases coexist due to microscopic compositional variations or internal stresses within the ceramic.

Because it is precisely the structural instability between these two structures that gives rise to the high piezoelectric activity in PZT, the useful compositions lie within or near this boundary region. Near this region, material properties vary rapidly with small changes in composition; this makes reproducing material properties from batch to batch a delicate balance. Moreover, the width of this boundary region (from 0.5 to 2.5 percent) depends critically on the synthesis technique and subsequent processing.

Thus, material parameters can vary 10-20 percent from nominal specifications in standard-grade piezoceramics, while small batch, expensive synthesis regimens lead to greater reproducibility, say 5 percent. The discussion identified no clear routes to the highly precise levels of reproducibility desired by the users.

Greater reproducibility in piezoceramic properties is not just an unreasonable desire of the users. The need to "trim" each device in production required high-cost, handicraft manufacturing methods. Even the design phase of devices encounters serious problems with ceramic property reproducibility. For example, to recalculate a device design using just three values—the nominal, one high, one low—for each of the 10 material constants of a piezoceramic (5 elastic, 3 piezoelectric, and 2 dielectric) requires more that 50,000 analyses, an impractical task. Experience and intuition must be used to guide the design to avoid device structures whose performance would be unreasonably sensitive to the range of material parameter variations. Tighter tolerance would make this task significantly easier.

The workshop identified a clear desire to use modern finite-element analytical techniques for device design. The increasing speed and decreasing cost of such computation makes this goal reachable in the near future. However, the workshop identified two barriers to the realization of this potential:

- accurate material parameters for input, and
- a versatile finite-element software package.

The material property question extends beyond the reproducibility issue discussed above to embrace the need for systematic methods and standards for material specifications. As a minimum, nominal values and ranges are needed for each of the 10 piezoceramic parameters. In addition, imaginary components (losses) and any pertinent frequency, temperature, field amplitude, and stress amplitude dependence must be documented for each material parameter. Standardized protocols to evaluate needed values as well as the widespread practice of carrying out a full set of measurements are prerequisites to efficient computerized device design. Quantification of the cost of such evaluation depends on the measurement standards to be implemented, but it clearly is not an incidental expense.

A versatile, modularized, modifiable finite-element code was a clearly stated need for efficient computer device design. An estimate of the cost to build such a software package was 60 professional years. The number of potential users was estimated to be a 100 or so, making the pro rata cost quite modest in terms of what it takes to go it alone, but making it quite expensive in terms of a laboratory's typical software budget. To resolve this issue requires only money.

PIEZOPOLYMERS

It has been more than 20 years since the discovery of the remarkable piezoelectric properties of

polyvinylidene fluoride (PVDF) polymers. Piezoelectric PVDF polymers are now recognized as materials with highly attractive properties for numerous applications including underwater sonar transduction. Piezoelectric PVDF polymers typically consist of long chains of monomer units of vinylidene fluoride. The polymers are known for their conformability, good acoustic matching with water, stability to corrosion, and, importantly, low cost. These properties make these materials ideal candidates as piezoelectric elements for underwater acoustic sensors and projectors. Transforming PVDF raw polymer into active and high-performance piezoelectric material is the key issue facing the polymer chemist and engineer.

"Electroprocessing" is the term applied to the mechanical and electrical procedures that convert raw PVDF from an inert material to a piezoelectrically active polymer. Normally, mechanical stretching and poling in a strong electric field transforms PVDF into a semicrystalline, piezoelectric material. It is now widely accepted that mechanical stretching plays a major role in inducing formation of the desired piezoelectric crystalline phase. Electroprocessing conditions must be carefully designed to achieve sufficient crystallinity, which is directly related to piezoelectric performance.

It was emphasized during the conference that a number of approaches are available to enhance the piezoelectricity of PVDF. Discussion centered on identifying suitable mechanical and poling conditions for converting thick-film PVDF into high-performance piezoelectric material for underwater arrays. Voided and ultra-high drawn PVDF poled in a direct electric field at ambient temperatures appear to be the best PVDF materials in terms of properties that satisfy Navy requirements for performance and sensitivity. One of the salient features of ultra-high drawn PVDF is enhanced thermal and mechanical stability. These properties are important for underwater sonar transducer applications. There was also discussion of the vinylidene fluoride-trifluoroethylene copolymers, which like the more "traditional" PVDF, can be made piezoelectric. The copolymers can be cast from the melt or solution. When annealed, the copolymer crystallizes into the desired crystal phase without the need for mechanical stretching. Thus, unlike PVDF, the copolymers can be cast into molds of almost any desired shape before poling. The degree of crystallinity of the copolymers can be controlled by selecting suitable annealing conditions.

The primary thrusts of the European piezoelectric materials community appear to be in synthesis and in improving the processing conditions for achieving sensitive and stable PVDF polymers and copolymers. Processing issues are also of interest to PVDF investigators in the U.S., although there is no U.S. manufacturer of piezoelectric PVDF and copolymers. The European community seems to be actively involved in several novel applications including, for example, the use of PVDF bimorphs for neural regeneration. When compared with their European counterparts, the American community appears to be more focused on the tailoring and synthesis of new classes of piezoelectric polymers such as the nylons. The nylons do not yet appear to be suitable for underwater sonar applications.

PIEZOCOMPOSITES

An extensive amount of composite transducer development was presented, especially in the areas of the so-called 0-3 and 1-3 techniques ("0-3" refers to piezoactive particles mixed randomly in the matrix; "1-3" refers to rods or pillars of piezoactive material oriented in the same direction in the matrix). These are based on work done at Penn State and at ONR in recent years. These composites hold potential, based on the fact that they use piezoelectric ceramics in combination with plastic and elastomeric materials. Such composites can provide performance similar to the parent ceramics, with the advantages of lower density, less weight, more complex shapes available, and better acoustic coupling to water. A novel technique for producing a 1-3 composite by means of the lost mold method was described. It involves filling a fugitive material honeycomb wall matrix with a ceramic slurry and drying, followed by burnout of the walls and sintering of the slurry. The resultant ceramic is backfilled with a polymer to form a conventional 1-3 composite.

Some participants have done some work in the area of fabricating 0-3 composites by using lead

titanate and nitrile rubber. Electrical conductivity of the composite was controlled by the use of carbon black.

Other work was described on 0-3 and 1-3 composite piezoelectrics. They have produced 0-3's on a near-production basis by using various resins and electroding materials. The result appears to be products ranging from rigid epoxies to flexible elastomerics with flexible electrodes. The products appear to be comparable in performance properties to the piezorubbers used in the past that came from Japan.

The latest developments in research, development, and fabrication of injection molding of 1-3 composites were described. Much of this work is proprietary, but a major university effort shows interesting parallels to work being done in the U.S.

MANUFACTURING PROCESSES

There is an underlying relationship between the performance of piezoelectric ceramics and the process for making the powder precursors. Several papers were presented on techniques for producing powders of high purity and fine particle size, including:

- spray pyrolysis of alkoxy precursors,
- low sintering powder techniques.

These techniques are all aimed at producing ceramics with small grain size and high purity and at obtaining the enhanced piezoelectric properties normally associated with these raw material properties.

In the spray pyrolysis process, organic liquid ceramic precursors are sprayed as an aerosol into a reaction furnace. There the particles of liquid are converted, one for one, into barium titanate powder. The droplets are 2-3 microns in size, and result in particles in the range of 0.5 microns. Although high in purity, the product does include some byproducts of the organic precursors, but these are separable and not intragranular.

Hydrothermal synthesis promises to permit a more economical approach to fine-particle, high-purity piezoelectric ceramics. This process uses precursors of lower cost than the organic reagents needed for other so-called "wet" processes. Nitrate salts of lead, samarium, manganese, and the oxide of titanium are mixed with NaOH and precipitated in a high-pressure, high-temperature reactor in an aqueous medium. The result is a single crystal powder of submicron particle size. The advantages include low cost, reproducibility, elimination of calcining and milling, lower sintering temperature, and improved compositional control. The full phase equilibria and solution chemistry is not yet known for all aspects of this process. The technique is available for a broad range of standard and ferroelectric ceramics.

An interesting variation on this theme is the electrochemical process, in which the reactor is fitted with electrodes. A desired substrate can be used as an electrode, and powder is uniformly deposited for subsequent firing into a thin film of high uniformity.

Other researchers reported on the hydrothermal reaction, along with high energy milling, chemical precursor synthesis, coprecipitation, sol-gel, and emulsion techniques, and hot pressing. The objective was to achieve low-temperature sintering products for multilayer actuators, ferroelectric thin films, and better properties by small grain size. Each process has its advantages and disadvantages with respect to product quality and cost. The processes are principally superior where performance of the final product is required, with less requirement for low cost.

The advantages of using low sintering materials in the fabrication of stacked wafer transducers were also described. By using the low-temperature sintering powders, electrode layers made with lower cost Pt-Ag layers can be used by cofiring entire stacks by hot pressing.

NOVEL APPLICATIONS

Three papers described some interesting uses for piezoelectric materials: piezoelectric motors, resonant piezoelectric sensors, and biomedical uses of piezopolymers.

Piezoelectric Motors

Research into using piezoelectrics as motors appears to have started in the former U.S.S.R. in the 1960s. The German company Siemens obtained several patents in the 1970s, and a Japanese camera incorporating a piezoelectric autofocus lens

motor has recently been put on the market. Piezoelectric motors offer the following advantages:

- high torque at slow speed;
- high holding torque;
- no magnetic signature;
- precise, continuous positioning;
- flat, thin, lightweight construction; and
- silent operation.

The concept of operation is that a flat array of piezoelectric elements forms the "stator" of the motor. This array can be either circular or linear to produce rotational or linear motion, respectively. An electronic control circuit applies phased voltages to the elements to produce traveling flexural waves on the surface of the stator. A flat plate (the "rotor") is held in frictional contact with the peaks of these flexural waves. Analogous to waves in the ocean, a given point on the surface of the stator moves in an ellipse as the wave passes. (n.b., the direction of motion of this point around the ellipse happens to be opposite in solids from that in liquids.) Thus, there is a horizontal component to the motion of the surface of the stator at the points where it is in frictional contact with the rotor (Fig. 1).

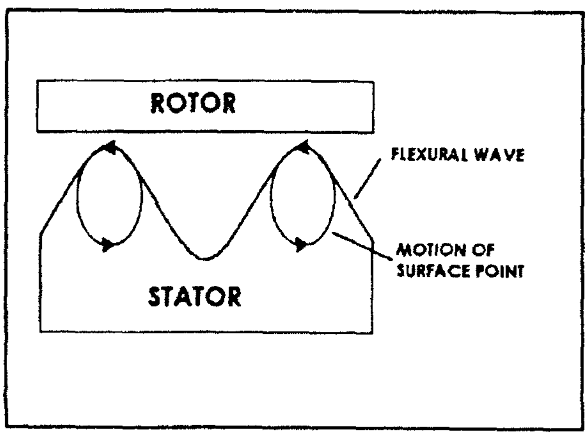

Fig. 1 - Example of piezoelectric motor array

Materials with high coefficients of friction (e.g., rubber) are usually used between the rotor and stator to maximize the torque produced. Unfortunately, these materials also tend to wear out, particularly in high torque applications. Extending the lifetime of these frictional elements is one of the principal technical hurdles facing piezoelectric motor designers.

Dr. Daniel Guyomar of Techsonic in France described a 5-watt, 6-cm-diameter motor he has built that develops 10 kilogram-meters of torque at 10 rpm, with a reported efficiency of 40 percent. Some commercial applications under development include automobile sunroof and window linear actuators, windshield wipers, and aircraft instrument displays.

Resonant Piezoelectric Sensors

Acoustic waves in solids are affected by a variety of environmental parameters, including temperature, pressure, mass loading, and acceleration. Miniature sensors are being produced that detect changes in the wave velocity or resonant frequency of vibrating piezoelectric elements that are induced by changes in these parameters.

Practical devices in current production include solid-state miniature gyroscopes and surface acoustic wave (SAW) chemical sensors. The principle behind the "no moving parts" gyroscope is that a resonant acoustic wave around a circular structure tends to maintain its orientation in space when the structure rotates about its axis. The SAW chemical sensors detect the change in resonant frequency of a vibrating element coated with an antibody that occurs when the specific antigen adheres to its surface. SAW sensors that sense temperature, stress/strain, pressure, acceleration, and humidity have also been developed. Additionally, Dr. David Hall of the University of Manchester, U.K., described some work to physically disconnect the tiny SAW sensor from its power supply and electronics, relying instead on inductive, capacitive, or radio-frequency (RF) coupling. This would be particularly beneficial in applications where there needs to be some relative movement of the sensor and/or a physical barrier is present (skin, for example).

The European efforts in this area parallel similar work in the U.S.

Biomedical Applications

The most surprising and intriguing biomedical application of piezoelectrics was the report by Dr. Claudio Domenici of the University of Pisa in Italy

that PVDF piezopolymers can, by themselves, induce severed nerves to reconnect. This cooperative research between the University of Pisa and the Artificial Organ Laboratory at Brown University in Providence, RI, has been reported in appropriate biomedical journals. However, very few of the piezopolymer chemists had heard of it.

ASSESSMENT AND RECOMMENDATIONS

The issues associated with piezoelectric device quality as a function of raw materials and fabrication processes were found to be very similar to issues identified in the U.S. Important properties of such devices are closely related to issues of materials purity and microstructure. Such properties include electromechanical coupling efficiency, activation displacement and force, reproducibility, and aging and reliability. Attention to raw materials and sub-device fabrication was repeatedly emphasized, as it is in similar exchanges within the U.S. Many of the approaches are based on information exchanges and even collaborations among researchers on both sides. Some need for information exchanges were also identified, wherein our researchers could benefit from their experience and vice versa.

Composite transducer materials on both sides appear to concentrate on the 0-3 and 1-3 concepts and their variants. Demonstrated 0-3's are nearing production in the U.K., and the U.S. has no comparable development. Because these composites have a potential for relative low cost and good performance, there is interest in adapting this technology. GEC-Marconi Materials Technology Limited, a British company leading in this area, has stateside manufacturing facilities and has begun preliminary efforts to establish their technology in the U.S.

Injection molding of 1-3 composites appears to be proceeding in parallel on both sides of the Atlantic. Recent ONR-sponsored work has resulted in U.S. progress that appears well ahead of what was presented here. Some collaboration could prove useful to both sides.

European piezopolymer research seems to be concentrating on improving the performance and manufacture of PVDF, while researchers in the U.S. appear to be more concerned with developing new classes of piezopolymers. Both European and American transducer designers strongly desire a Finite-Element Methods/computer-aided design package tailored for piezoelectrics. The large size of this task compared with the relatively few potential customers worldwide makes this an excellent candidate for international collaboration.

Abstracts and viewgraphs from the international meeting are available from the Office of Naval Research European Office ("Piezoelectric Materials Research in Europe," ONR Europe Report 93-7-R).

Sol-Gel Processing Science In France

by Mufit Akinc, Liaison Scientist for Materials Science at the Office of Naval Research European Office. Dr. Akinc is on leave from Iowa State University where he is Professor of Materials Science and Engineering.

KEYWORDS: sol-gel science; ceramic processing; France; academic research; spectroscopy

INTRODUCTION

Sol-gel processing has been one of the most popular topics of research in ceramic processing during the past decade or so. In Europe, French scientists are very active in this area, and their record has been impressive. Reference 1 describes recent general materials research in Europe. This article is limited to describing sol-gel research at academic institutions in France.

Sol-gel processing research in France is primarily supported and coordinated by the Centre

National de la Recherche Scientifique (CNRS). Advanced materials research is carried out by universities, national laboratories, and industry and shows specific strengths. Particularly noteworthy is sol-gel processing of single and multiphase oxides, advanced composites based on carbon and SiC.

Sol-gel processing research has gained an unprecedented popularity in the world research community over the past decade. Ceramists, chemists, and physicists have worked on different aspects of the process to formulate new compounds, as well as to better understand and optimize existing processes. For the most part, silica-based compositions are considered for structural, chemical, and protective applications; transition metal oxides are candidates for electronic and magnetic applications.[2]

In a broader sense, the sol-gel process refers to the formation of small clusters (sols, where Brownian motion dominates over gravitational forces), followed by linkage of these clusters to form a more-or-less continuous framework (gel, gelation where translational motion is greatly hindered within the solvent), and finally followed by removal of the solvent. Literature has generally been limited to one type of sol-gel process: hydrolysis of metal alkoxides in alcoholic solutions. This is also true for the sol-gel processing research in France. The process has two major steps: hydrolysis of alkoxy groups, followed by condensation of hydroxy groups to form oxides. In hydrolysis, the rate-determining step is the hydrolysis of the first alkoxide group. Once the first alkoxide is exchanged for one OH group, the second, third, and fourth alkoxide groups hydrolyze much more rapidly. This leads to a complete hydroxylation and is followed by a much slower process, condensation.

RESEARCH AT ACADEMIC INSTITUTIONS

Overview of Research Laboratories

The research into sol-gel processing in France is impressive. This may partly be due to the longtime research strength of France in glass and spectroscopy. In the past decade, more than 20 academic institutions and probably more than 10 industrial research and development (R&D) laboratories have been involved in sol-gel processing research. More than 100 permanent research scientists are employed in sol-gel research.[3] When technicians and graduate students are included, the total number of people working at the academic CNRS institutions reaches about 300 people. Research in sol-gel processing is supported and orchestrated by the CNR and is carried out under two major groups ("grecos," Groupement de Recherches Coordonnees). The first group deals with "molecular precursors," which primarily refer to small chemical units; the second group deals with "glasses," which encompasses everything from gels to dense glasses (high-temperature behavior, etc.).

A benefit of a single-source support and umbrella organization is that coordinated and well-planned research programs can be executed. This avoids the fragmented and overlapping (sometimes duplicative) research efforts that are often seen in the U.S. These two grecos also serve as a forum for communication among scientists working on related problems. To facilitate this interaction and review research progress elsewhere, summer schools (a combination of symposia, workshops, and short courses) are held regularly. So far, three such summer schools (1987, 1989, and 1991) have been held. The fourth one is scheduled for 19-23 July 1993 in Paris.

Sol-gel processing research carried out in academic institutions in France is described in the following sections. Since it is impractical to discuss every research activity, only those projects are discussed for which the author was provided (or had access to) relevant information, or areas with which the author is particularly familiar. Research done by industrial laboratories is not included in this article, but the work supported by industry in academic institutions is mentioned wherever appropriate. The following section provides the titles of current projects at academic institutions in France.

Laboratoire de Chimie Moleculaire — L.G. Pfalzgraf

- Design of Molecular Homometallic precursors
- Design of Heterometallic Precursors

Laboratoire des Precursors Organometalliques de Materiaux — R. Corriu
- Polysiloxane Gels
- Mixed Organic-Inorganic Polymers
- Metal Oxides via non-Hydrolytic Routes

Laboratoire de Chimie Organique et Organometallique — J. Dunogues
- Precursors of Hybrid Organic-Inorganic Gels
- Ferroelectric Ceramics by Sol-gel

Centre d'Elaboration de Materiaux et d'Etudes Structurales — A. Mosset
- Transition Metal Alkoxides

Laboratoire de Chimie de la Matiere Condensee — J. Livage
- Molecular Design of Alkoxide Precursors
- Inorganic Polymerization in Aqueous Solutions
- Physical Properties of Oxide Gels

Laboratoire de Physique de la Matiere Condensee — J.P. Boilot
- Aluminosilicate Fractal Aerogels
- Sol-gel Transition and Aging of Silica-based Gels
- Sol-gel Route to High-Performance Ceramics
- Sol-gel Matrices

Laboratoire de Science des Materiaux Vitreux — R. Vacher
- Structural and Vibration Modes of Aerogels
- Mechanical Properties of Silica Gels and Aerogels
- Mixed Silica Aerogels
- Partially Densified Aerogels-Host Material
- Sonogels

Laboratoire de Physicochimie des Materiaux Luminescents — M. Romand
- Physical Properties of Inorganic Gels, Aerogels, and Glasses
- Structural, Textural, and Mechanical Properties of Monolithic Oxide Gels
- Ceramic Coatings on Metallic Substrates

Laboratoire de Physicochimie des Materiaux — L. Cot
- Fundamental of Sol-to-Gel Transition in Reversed Micelles Microemulsion
- Modification and Hydrolysis of Metal Alkoxides
- Nanomaterials Prepared by Sol-Gel Processing
- Organic Inorganic Composite at the Molecular Levei
- Ultrafiltration and Nanofiltration Membranes
- Catalytic Membranes
- Powder Elaboration
- Superconducting Materials

Laboratoire d'Ionique et d'Electrochimie des Solides — C. Poinsignon
- Ormolytes as Polymer Electrolytes
- Ceramic Elaboration for Sensors
- Mixed Oxides as Transparent Materials for Electrochromic Windows

Groupe des Materiaux Inorganiques — J.C. Bernier
- Ceramic Powders
- Sols and Colloidal Suspensions
- Study of Sol-gel by Electrochemistry

Laboratoire de Ceramiques Nouvelles — A. Dauger
- Ceramic Precursors and Nanostructure
- Nucleation in Glass Ceramics
- Colloidal Precursors for Ceramic Materials

Centre Recherche sur la Physique des Hautes Temperatures — P. Odier
- Superconducting Oxide by Solution-gel Polyacrylamide Route
- Dielectric Materials by Citrate Process (Pechiney)

Laboratoire Chimie du Solide du C.N.R.S. — R. Salmon
- Dielectric and Ferroelectric Materials
- Fine Spherical Particles by Aerosol Technique

Groupe de Radiochimie, Institut de Physique Nucleaire — M. Genet

- Transparent Phosphate Xerogels for Optics

Research at Laboratoire Chimie de la Matiere Condensee — J. Livage

Sol-gel research at this university is probably the largest effort in France—about 40-45 people here are working in this field. This includes scientists (~15), technicians (~6), and graduate students (~20). Professor Jacques Livage, who heads this group, is also chairman of the sol-gel research activity of CNRS in the Paris region and chairman of the French Sol-Gel Group. Professor Livage and his group are working in molecular precursors. Because they are chemists by training, almost all of the research they do involves a heavy dose of chemistry and spectroscopy.

A major portion of their work is in the area of the alkoxide chemistry. A small but significant effort in hydrolysis of cations in aqueous media is also being carried out at the University of Pierre et Marie Curie (P&M).

Molecular Design of Alkoxide Precursors

The scientists at P&M are studying the modification of the alkoxide precursor molecules by substituting carboxylic acid or other organic groups for one or more of the alkoxides. Depending on the nature of these substituents, organic components may either be embedded in the gel matrix or chemically bonded to the metal oxide backbone. These hybrid (inorganic-organic) polymers are likely to open new avenues for electronic and/or optical applications. If the organic chelates are polymerizable themselves, then a metal-carbon backbone in the polymer is obtained, which may be considered to be precursor to oxycarbides, oxynitrides, or oxycarbonitrides for structural ceramic applications.

Although studies are primarily concerned with "ormosils" (organically modified silicates), the basic principles are applicable to a variety of metal oxides, in particular, transition metal oxides. The research involves the polymerization of alkyl substituted alkoxides $R'_xM(OR)_{4-x}$ where M is a quadrivalent metal atom (Si, Ti, Zr, etc.), R and R′ are alkyl groups, and $x \leq 2$. These polymers are receiving considerable attention as a matrix for optical or electromagnetic nano composites. In some cases, these alkyl substituted alkoxides are reacted with other metal alkoxides to form copolymers of greater chemical complexity than would otherwise be impossible to produce.

Primary advantages of the ormosil approach are twofold: first, by reducing the functionality of the monomer from four to three, or even lower, the polymerization reaction is better controlled, and tractable polymers are obtained. Secondly, these monomers provide inorganic-organic hybrid polymers that have interesting applications at ambient temperatures. As mentioned above, these hybrid polymers can also serve as precursors to high-temperature ceramics when pyrolyzed. The capability to alter the nature and fraction of alkyl groups will enable a variety of oxycarbides, oxynitrides, and oxycarbonitrides to be synthesized.

Research into the synthesis of multi-metal ormosil systems is rigorous and at the cutting edge, but the area is in its infancy. For instance, it is not known whether Si-O-M bonds actually form, or whether they form nanoscale aggregates of MO_x in the matrix of $R_xSiO_{2-x/2}$. Not much is known about the short-range environment of these metals; the polymerization process is being characterized. For this, EXAFS (extended X-ray analysis of fine structures), high-resolution MAS-NMR (magic-angle spinning-nuclear magnetic resonance), SAXS (small-angle X-ray scattering), SANS (small-angle neutron scattering), XRD (X-ray diffraction), and FTIR (Fourier transform infrared) spectroscopic techniques are being extensively used.

Inorganic Polymerization in Aqueous Solutions

The alkoxide hydrolysis route has been popular with the research community in the past decade or so. However, the aqueous route to oxide powders and monolytic bulk pieces of complex compositions is more advantageous if the composition, structure, and morphology can be controlled. The aqueous route is generally preferred by industry because the starting materials are much cheaper, easier to handle, and environmentally safe. It has the disadvantage that although it appears to be straightforward, hydrolysis of cations in aqueous solution is extremely complicated. Complex intermediates are usually formed, and the reaction mechanisms are

hardly describable, despite the vast amount of literature available for specific systems.

Professor Livage and his group (primarily, Dr. Marc Henry) developed the so-called Partial Charge Model to describe, and to some extent predict, the hydrolysis, complexation, and condensation processes in aqueous solutions. The method is based on equalization of electronegativity of various species in the solution. It actually is an extension of the principle of Sanderson, which states that when two or more atoms of different electronegativity are brought together, they approach a common electronegativity value in the compound.

Starting with relatively simple equations based on electrochemical potentials, Prof. Livage and his group were able to generate:

- a charge-pH diagram, which explains the hydrolysis of cations in the aqueous media;
- a charge-electronegativity diagram, which predicts the type of condensation that a cation is expected to undergo; and
- an electronegativity-pH diagram, which accounts for the complexation of the cations under consideration.

The charge-pH diagram shown in Fig. 1 predicts that at high pH, high charge region oxo ions will be stable, whereas low pH, low charge region hydrate (aquo) species will be stable. Between these two is an intermediate domain that corresponds to a stability range for hydroxide species. Since condensation requires at least two hydroxides per cation, the condensation reactions occur in this intermediate region. Experimental data are in good agreement with these predictions. Figure 1 shows that the pH must be increased for the mono- and divalent cations to form precipitates, whereas multivalent cations are precipitated by either decreasing pH or reducing the valency of the cation.

Figure 2 shows a charge-electronegativity diagram with a number of elements labeled. According to this diagram, one can predict, for a given element, if it forms hydroxide, oxide, or polyacid, or remains as a dissociated cation. For instance, elements having very low electronegativity form inorganic bases that do not undergo condensation reactions (Na, Ba, Ca, etc.). Elements with very high electronegativity undergo acidic dissociation, forming oxyanions; these are also stable in solution. On the other hand, elements with low electronegativity undergo olation (oxidation), leading to hydroxide; those with high electronegativity form polyacids. Elements with electronegativity between these (i.e., intermediate electronegativity) form hydrous oxides $M_{z/2}O \bullet xH_2O$.

Use of these diagrams greatly simplifies finding the types of complex ions that form and condensation paths that are conceivable when a metallic salt is dissolved in an aqueous solution. The method is powerful and predictive, but unfortunately only semiquantitative. A significant amount of work has yet to be done to incorporate the concentration of cations, temperature, pressure, and ionic

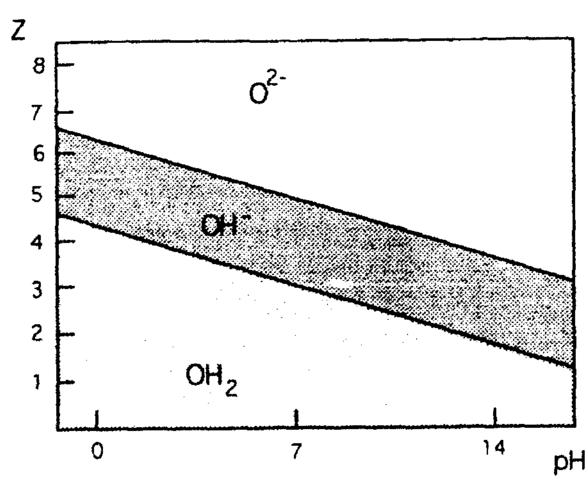

Fig. 1 – Charge-pH diagram

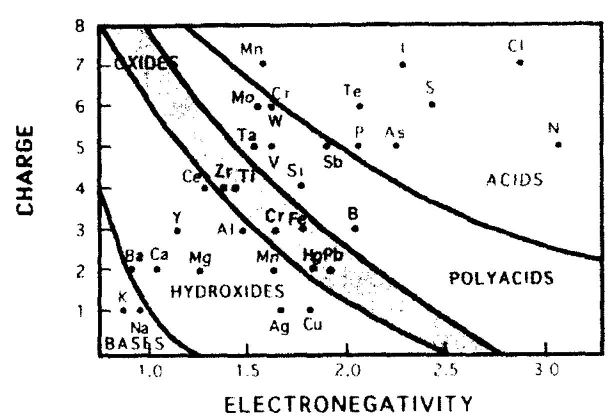

Fig. 2 – Charge-electronegativity diagram

strength. Another shortcoming of this theory that it is phenomenological and does not predict the spatial arrangement of the atoms in the complex. Doctor Marc Henry is currently working on this problem by using NMR spectroscopy.

Research at Laboratoire de Physique de la Matiere Condensee — J.P. Boilot

Ecole Polytechnique was established in 1794 to train scientists and engineers for the military. Over the years it has broadened its mission to train scientists and engineers for the government and industry as well. Ecole Polytechnique is still considered to be one of the premier technical institutions in France.

The research center of the school has 24 laboratories, 10 of which are physics laboratories. Sol-gel processing science is carried out in the condensed matter physics laboratory along with groups in fractals, semiconductor/electrolyte interface, photo emission, and nuclear magnetic resonance.

In addition to its core support from CNRS, the laboratory gets support from and collaborates with industry. Some of the industrial partners are Thomson-CSF, Elf-Aquitaine, Saint-Gobain, Solems, and Pechiney.

The sol-gel research activity at Ecole Polytechnique is headed by Prof. J.P. Boilot, an extremely talented scientist. The majority of support is derived from CNRS, but significant financial support is also derived from industry. The group consists of about 10 scientists, including post-doctoral associates, technicians, and graduate students. Ecole Polytechnique is one of the best institutions in sol-gel processing research in France.

Several investigations into alkoxide chemistry are being undertaken. These include:

- silica and aluminosilicate fractal aerogels,
- kinetics of sol-to-gel transition and aging of silica-based gels,
- sol-gel processing of electric/electronic ceramics, and
- nano composites for optical and electromagnetic applications.

It is interesting to note that although a large number of projects are being carried out, they all form a coherent program around processing and characterization of silica-based gels.

Fractal Aerogels

Fractal aerogels based on silica have been synthesized and investigated in the U.S. and elsewhere. Professor Boilot's group is investigating such fractals to understand the mechanism of gel formation in acid-catalyzed silica and aluminosilicate systems. They have very practical motivations for investigating fractal aerogels. These aerogels exhibit extremely low density, thermal conductivity, sound velocity, and in many cases good optical transparency. These unusual properties open up a variety of applications, including transparent insulators, catalyst supports, gas absorbers, and acoustic delay lines.

Since the fractal units range from 1 to 100 nm (depending on the density), a particular mode of excitation in these materials is local vibration of the fractal units called "fractons." Fractons do not allow sound or heat to propagate over long distances. The aim of Prof. Boilot's group is to investigate structural and dynamic characteristics of fractal aerogels from the starting monomers through the gel state.

Based on NMR, SAXS, and SANS data they came up with following conclusions:

- A high level of condensation (0.81) takes place prior to gelation, indicating that highly condensed agglomerates form, rather than random polymerization of the monomers, which would exhibit gelation at a condensation value of 0.5.
- The condensation process itself is not random but involves step by step assembly leading to small but more-or-less ordered clusters.
- Aggregation of small clusters starts at a condensation value of about 0.6.
- SAXS measurements indicate that the fraction of the clusters at gel point approach unity. This takes about 50 days at room temperature. At this stage the radius of gyration is about 5 nm. The aggregation kinetics is assumed to be reaction-limited cluster aggregation (RLCA), not diffusion controlled.

- Different alkoxide:alcohol:water ratios gave rise to the same structure at the gel time, indicating that hydrolysis reaction is rapid and complete compared to condensation reaction.
- Comparing the static- and magic-angle spinning (MAS) spectra implied that rotational motion of the gel progressively freezes. It is claimed that the gel transition occurs via formation of a large-scale percolation cluster coexisting with small clusters that slowly connects to large structures.

Most of their findings are confirmed by independent techniques on identical samples, giving more credibility to the offered mechanisms. Their work supports the initial work of Shaeffer and O'Keefe but the present investigation is more complete and extensive.

Preparation of Nano-size Clusters of CdS in Silica Gel Matrix

Nano-size clusters have received much attention recently; these materials exhibit nonlinear optical properties resulting from quantum confinement effects. To observe the quantum (Q) effect, the particles must be small and have narrow size distribution. Semiconductor-doped glasses are important for applications such as shutters, waveguides, and optical switches.

Professor Boilot and his graduate student are investigating synthesis and dispersion of nanoscale CdS clusters in a silica matrix. In this study, nano-size CdS clusters are chemically synthesized by using direct precipitation, γ-radiolysis, and inverted micelles techniques.

In this article we review the synthesis and processing of the CdS clusters by the inverted micelles technique. The inverted micelle was prepared by a process similar to water-in-oil emulsions using aqueous solution of $CdCl_2$, surfactant aerosol AOT (sodium di-2-ethyl hexylsulfosuccinate), and heptane as the oil phase. Precipitation of CdS is accomplished by passing H_2S through the micelle. Removing the CdS cluster formed in the micelles and dispersing them in silica gel is not a trivial exercise. The scientists at Ecole Polytechnique accomplished this by adding phenyl thiol (C_6H_5-SH) solution in heptane to the micelle. Thus phenyl-capped cadmium sulfide clusters can be separated from the aqueous solution without aggregation. The CdS clusters obtained by this technique have a narrow size distribution. Clusters having a mean size of 1 to 5 nm can be obtained with a standard deviation of 0.15. The capping of the CdS clusters now has to be exchanged again so that they can be dispersed in silica gel. This is achieved by a mercaptoalkoxide, namely 3-mercapto propyl trimethoxysilane, which is referred by the investigators as "magic thiol." This reagent acts as a bridge between the CdS clusters and the silica gel in which the CdS clusters are dispersed. Dispersion is readily obtained by stirring magic thiol-capped CdS in alkoxide sol; the sol is then aged to form the gel. Further gelation in the ambient atmosphere for an extended period of time results in dense xerogel with a glassy appearance. Optical absorption, SAXS, XRD, and HRTEM observations confirm that the clusters remain unaggregated throughout the process and the mean size of the clusters are about 2.5 nm and 5 nm for two typical sets of experimental conditions. The CdS-dispersed xerogels exhibit a broad emission spectrum—between 500 and 700 nm for a 355-nm radiation.

Alhough not discussed here, samples of PbS were also prepared in this study. There is no reason why this technique cannot be applied to other sparingly soluble transition metal chalcogenides.

Processing Perovskite Dielectrics for Microwave Applications

Boilot's group is also studying novel processing of barium magnesium tantalate ($Ba(Mg_{1/3}Ta_{2/3})O_3$) dielectrics. This and other perovskite structures are being considered as dielectric resonators for stabilizing oscillators or for frequency filters. For miniaturization, the material should have high dielectric permeability, low dielectric loss, and small temperature coefficient of resonant frequency. Pure and dense barium magnesium tantalate (BMT) shows an excellent dielectric constant (about 36,000 at 10 GHz), which makes it the material of choice for microwave applications.

Boilot and his coworkers were able to synthesize very fine, homogeneous BMT powders by

reacting heterometallic magnesium di tantalum ethoxide ($Ta_2Mg\ (OEt)_{12}$) with hydrated solid barium hydroxide ($Ba(OH)_2 \bullet 8H_2O$). Hetero-metallic alkoxide was first prepared by reacting $TaCl_5$ with ethyl alcohol in an ammoniacal hexane solution followed by reaction with metallic magnesium in alcohol. The reaction sequence is summarized as:

$$2TaCl_5 + 10EtOH + 4NH_3 \xrightarrow{EtOH} (Ta(OEt)_5)_2 + 4NH_4Cl + 6HCl$$

$$(Ta(OEt)_5)_2 + Mg + 2EtOH \longrightarrow Ta_2Mg(OEt)_{12} + H_2$$

$$3Ba(OH)_2 \bullet 8H_2O + Ta_2Mg(OEt)_{12} \longrightarrow Ba_3MgTa_2(OH)_{18-x}(OEt)_x$$

Heat treatment of this precursor to $T < 700°C$ results in a homogeneous, single-phase BMT powder with a particle size of about 100 nm, albeit aggregated. These powders are sintered at 1400°C in air atmosphere to produce dense parts (98.5 percent of theoretical). Dielectric properties of the material are currently being studied.

This technique is applied to synthesis of barium zinc tantalate (BZT) powders as well. In this case, zinc alkoxide is used as the cation source rather than the metallic magnesium used in the above reaction scheme.

Tritium Release from Lithium Silicate-Based Ceramics

Lithium ortho silicate and related materials are to be used as nuclear fusion blanket materials. Although the primary purpose is not the processing of lithium silicate ceramics, they have synthesized and processed a number of lithium aluminosilicate and lithium phosphosilicate gels at various levels of Al and P substitution to change the lithium ion mobility. The process involves synthesizing lithium silicate by the alkoxide hydrolysis route. In the process, Li is added either as lithium butoxide (in pure lithium silicate) or as LiOH (in lithium silicate doped with aluminum or phosphorus). Professor Boilot's investigation revealed that the tritium release does not depend on the adsorption/desorption process. They also found that the slight excess of LiOH enhances the tritium release through higher concentration of the OH groups on the pore surfaces or at the grain boundaries. Needless to say, the higher surface areas provided by the sol-gel process also contribute to higher tritium release by providing higher concentrations of OH for the adsorption and desorption.

The significance of sol-gel processing in this work is that the investigators were able to produce a variety of compositions with greater homogeneity, purity, and high surface area. This allowed them to assess the role of lithium ion conductivity on tritium release, which was insignificant. As a result, they were able to provide a plausible mechanism for the process.

Research at Laboratoire de Chimie des Solides — A. Revcolevschi

Sol-gel processing research at Universite Paris-Sud is not as extensive as at the other universities. The university is well recognized in the nuclear physics field. Materials research is being conducted in the Chemistry Department. Within materials research activities, there are four sections: metallurgy I, metallurgy II, solid state chemistry, and non-stoichimetric compounds. My understanding of the organization is that metallurgy I is supported by CNRS, while metallurgy II is supported by the university. Sol-gel processing research is being carried out in the solid state chemistry group which employs three CNRS-supported professionals and four university-supported personnel. Total budget for these activities is estimated to be around FF 1.0 M/year ($200K/year).

Most of the research in solid state chemistry involves characterization of the gels. Their primary concern is to understand the short order structure of the gels. In this area they are using a number of spectroscopic techniques, especially EXAFS, which they have on the campus. Among the materials being investigated are Al_2O_3-ZrO_2 composites. Doctor Berthet, a colleague of Prof. Revcolevschi, is trying to elucidate the form of ZrO_2 in these gel systems. The findings so far are inconclusive as to whether ZrO_2 is in a tetragonal or cubic environment.

A more interesting R&D area is sol-gel synthesis of Al_2O_3. They revisited the procedure developed by Yoldas of the U.S. In this process the alkoxide is hydrolyzed at about 80°C to form the

boehmite (AlOOH) sol. Sol is separated from the alcohol solution and peptized in HCl solution at 95°C for several hours. The investigators at Paris-Sud claim that by modifying the procedure (they don't tell how) they were able to peptize the sol at room temperature and in several minutes. They also repeated the same procedure with a commercial boehmite sol (Vista Chemical's Dispal) and got the same result.[4] This implies that the peptization procedure is modified, not the alkoxide hydrolysis. That of course brings the idea of either changing the acid type or content used in the peptization. It will be interesting to learn more about the details of the process in the near future. It is significant that lowering the temperature and time of peptization is not only advantageous in terms of ease of processing, but also that the crystallites produced under these milder conditions are much smaller and offer a potential ease of densification of these gels. The effort is not large enough to see such results soon. The activity is presently more concentrated on determining the influence of processing parameters on the critical gelation concentration and time to gelation.

Research at Centre D'elaboration de Materiaux et D'etudes Structurales — A. Mosset

This laboratory is funded fully by CNRS and operates within the molecular precursors framework. Sol-gel research at this institute is very much concentrated on the structural analysis of the crystalline (alkoxide) precursors and development of the gel structure. The precursors investigated are usually heterometallic, with silicon being one of the elements and the other usually being a transition metal. To improve the stability of the bimetallic alkoxide compounds, they introduce chelates such as acetylacetonates into the molecular structure. After crystallization, they characterize the precursors with respect to composition and structure. The primary tool they use in these investigations is large-angle X-ray scattering (LAXS).

Research at Laboratoire de Science des Materiaux Vitreux — R. Vacher

Sol-gel research at the vitreous materials laboratory is headed by Dr. Vacher. The group consists of 52 investigators (18 permanent scientists, 20 graduate students, and 14 technicians). This group's major source of funding is also from CNRS, but they have some additional support from and collaboration with industry. Having reviewed a large number of their publications and presentations, I came to the conclusion that they are collaborating with a number of other CNRS-supported laboratories. It appears that the majority of the research work is concentrated on silica-based aerogel processing and characterization. Among their research projects, evolution of microstructure and mechanical properties of aerogels with heat treatment has received a considerable emphasis. Partially densified aerogels are used as hosts for rare-earth compounds. These aerogels are being considered for magneto-optical applications. Specific optical properties are also obtained by doping silica with rare-earth cations. Professor Zarzycki, a principal scientist in this laboratory, is investigating the sonogels—gels that are produced by ultrasonic irradiation of the alkoxide and water solution. He claims that sonic irradiation catalyzes the hydrolysis and/or condensation reactions, and the gels obtained by this method exhibit different structure and properties.

Research at Laboratoire d'Ionique et d'Electrochimie des Solides — C. Poinsignon

This laboratory (LIES) is within the School of Engineering at the Polytechnique Institute of Grenoble. LIES is one of four research laboratories within the School of Electrometallurgy and Electrochemistry. They are known internationally in the area of solid state ionics. The laboratory employs a total of about 50 people (23 scientists, 8 technicians, and about 20 graduate students). Research into conducting materials encompasses both basic science and applied engineering (especially toward device development).

They investigate polymer electrolytes and inorganic ionic conductors (glasses and crystalline) as electrolyte and electrode materials.[5] These materials find applications in batteries, fuel cells, electrochromic windows, electrosensors, and other products. The sol-gel route to electrolyte and electrode materials is very attractive since the process allows forming thin coatings, membranes, and fibers.

The LIES-Grenoble has a concerted effort in ormolytes (organically modified ceramic electrolytes). These materials are produced by grafting organic functional groups to a silicate polymer network. Mechanical properties of ormolytes can be modified by altering the structure of the silicate backbone, whereas with hydrophobicity, electrical properties can be altered by the organic moeities attached to this backbone. It is worth mentioning that it is possible to polymerize the organic moieties to crosslink the silicate chains, thus improving the mechanical properties.

A number of electrolyte compositions have been investigated. Poly-(benzyl sulfonic acid)-siloxane (PBSS) membrane was prepared by hydrolysis and condensation of triethoxybenzylsilane. The condensation product is then sulfonated. This material shows a good oxidation resistance and is being considered as an alternative to polymeric solid electrode materials in fuel cells.

Another material under investigation is aminosil. This material is also based on sol-gel processing of siloxanes with amino groups attached to the backbone. Conductivities on the order of 10^{-5} S cm^{-1} were obtained at room temperature. Sulfonamidosil is another ormolyte that the LIES group has investigated. The polymerization process is somewhat complicated. Sulfonamide-containing silicon alkoxide is copolymerized with an internal plasticizer. Professor Poinsignon and his coworkers were able to produce thin films that were homogeneous and transparent. Electrical conductivity in these polymers is due to proton vacancies. Maximum conductivity was observed when 15 percent of the sulfonamide groups are deprotonated. Conductivity values of 2×10^{-7} S cm^{-1} at room temperature and 1×10^{-5} S cm^{-1} at 84°C were reported. The polymers were stable up to 220°C.

The LIES-Grenoble group is also studying the influence of processing conditions on the electrical response of nasicon (Na super ionic conductor) materials. The chemical composition of this material is $Na_{1+x}Zr_2Si_2P_{3-x}O_{12}$. The optimum conductivity is found at $x=2$. They have investigated drying and sintering conditions to improve the electrical response of the material, but so far improvements are not very significant.

Another area of interest in the sol-gel processing is the CeO_2-TiO_2 system as a counter electrode in electrochromic windows. Because Li diffusion is rather slow in CeO_2, the group studied the addition of TiO_2 to "open-up" the structure for Li diffusion. The process involves hydrolysis of cerium and titanium butoxide in the presence of acetylacetonate. Optimum Li conductivity is observed at 50 percent CeO_2. The mechanism of the improvement is speculated but not well understood as yet.

CONCLUSIONS

Although use of metal alkoxides, either by pyrolysis or by hydrolysis, had been known for more than 40 years, the method did not receive much attention until the 1980s. In the last decade, research has accelerated tremendously. The number of scientific articles published in the last decade is in the thousands. Similarly, a Japanese survey indicates that 1300 patents were issued in the last ten years.[6] It is interesting to note that despite the explosion of information in this area in the past ten years, there is not much to show in terms of industrial implementation. It appears that the high cost of this process precludes the commercialization of the process in all but a few cases. Because of the high purity and homogeneity of the materials produced, the alkoxide route could become commercial in electronic and magnetic applications, particularly in micro systems and in the form of thin films where low volume, high value-added products can justify the cost of the material.

Looking back to materials that are being investigated in France, one finds that there are actually two types of investigations. The first group is studying the fundamentals of the synthesis and hydrolysis of alkoxides. In these studies we generally see that materials of choice for investigation are those containing Si, Ti, and Al. The second group is somewhat product-oriented; hence, compositions for electronic, magnetic, and optical applications are favored. Among those, compositions based on spinal structure, numerous compositional variations of perovskite structures, and amorphous or isotropic materials for optical applications are being investigated.

Sol-gel research in France is heavily dominated by chemists. Consequently, research emphasis is on synthesis and precursor characterization. Sintering does not appear to be strongly emphasized in academic institutions. It is probable that high-temperature work is being done at the industrial laboratories.

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New Basic Materials and Applications of Electronically Conducting Polymers Highlighted at Swedish Synthetic Materials Conference

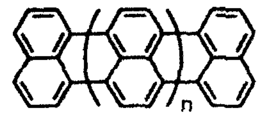
by Kenneth J. Wynne, Chemistry Division, Office of Naval Research, Arlington, VA; Martin Pomerantz, Center for Advanced Polymer Research, Dept. of Chemistry, The University of Texas at Arlington; and John R. Reynolds, Dept. of Chemistry, Center for Macromolecular Science and Engineering, University of Florida, Gainesville.

KEYWORDS: conjugated polymers; electrochemistry; properties; processability; intrinsic conductors

INTRODUCTION

The International Conference on Science and Technology of Synthetic Metals (ICSM) is the primary international conference in the areas of conjugated, conducting polymers and charge transfer materials. ICSM '92 was held 12-18 August 1992 in Göteborg (Gothenburg), Sweden, and included Buckminsterfullerenes for the first time. Approximately 800 conference attendees from all over the world presented about 960 papers in various areas including conducting and electroactive polymers, organic superconductors, metal chalcogenides, Buckminsterfullerenes (buckeyballs), and nonlinear optics. Approximately half of the papers described research advances in the

chemistry, physics, and materials science of conducting polymers. Papers from the conference will be published in a special series of *Synthetic Metals* and is expected to be available by mid 1993. This report focuses on advances in the research on conjugated polymers, which include polyarylenes, polyanilines, poly(arylene vinylenes), polyacetylenes, and miscellaneous systems. These materials are either electroactive, conducting, or (as has been reported fairly recently), electroluminescent.



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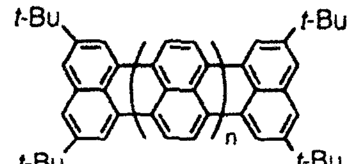

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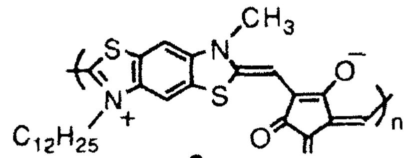

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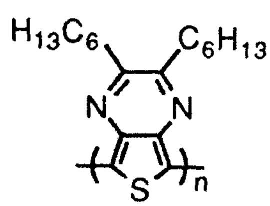
NEW POLYMERS

A number of important directions continue to be pursued in the synthesis of new polymers with delocalized electronic states. One is improved processability. Polymers with delocalized electronic states tend to be "inflexible" chains that defy the attempts of researchers to obtain solutions or stable melts. Polymer solutions or melts are generally required to obtain useful forms such as films, fibers, and blends. In addition, new polymers are sought that have improved environmental stability, i.e., stability to air, water, and heat. Their use in applications such as composites, antistatic films, and batteries require such stability. In another direction, polymers are sought with low band gaps. Very low energetic requirements for the promotion of an electron from the valence band to the conduction band could result in polymers that are intrinsic conductors, i.e., behave "naturally" like metals. If such a class of polymers could be created, "doping" or partial oxidation would not be necessary, and the polymer could be used directly as a conductor.

Several interesting polymers that show exceptional thermal stability were reported by K. Müllen [Max Planck Institute, Mainz, Federal Republic of Germany (FRG)]; two of these are shown in structures **1** and **2**. A number of new low band-gap polymers were reported. One class, discussed by E.E. Havinga (Phillips Research Laboratories, Eindhoven, The Netherlands), is alternating copolymers of donor and acceptor groups; it was claimed that these have band gaps as low as 0.5 eV, the lowest band gaps yet reported. One of the molecules is shown in structure **3**. One of the authors (M. Pomerantz) reported on the synthesis and properties of poly(2,3-dihexylthieno[3,4-b]pyrazine) (**4**). It has a band gap of 0.95 eV [which is lower than that of poly(isothianaphthene)], is opaque blue-black when neutral (either in solution or as a film), and becomes a transparent light yellow when doped. S. Tanaka (Myodaiji, Japan) reported on the electrochemical preparation of polymer **5**, which has a band gap of about 0.9 eV. Two new derivatives of the low band-gap polymer poly(isothia-naphthene) (**6a**) have been reported. One of the authors (M. Pomerantz) reported on poly(5-decylisothianaphthene) (**6b**). This is soluble in organic solvents and, like the parent, is opaque blue-black when undoped and becomes transparent light yellow upon doping and has a band gap close to 1 eV. M.J. Swann (University of Durham, England) reported that the perfluorinated derivative **6c** (n ≈ 20) has a considerably higher band gap of about 2 eV. It was demonstrated both by Raman spectroscopy (H. Kuzmany, University of Wien, Austria) and NMR spectroscopy using model compounds (I. Hoogmartens, Limburgs University, Belgium) that poly(isothianaphthene) (**6a**) exists in the quinoid form **7**, as predicted by earlier theoretical quantum mechanical calculations.



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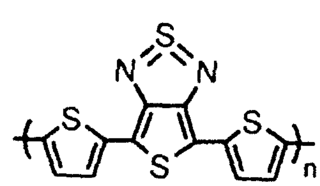

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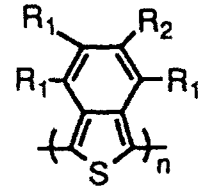
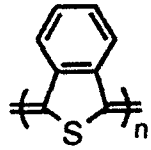
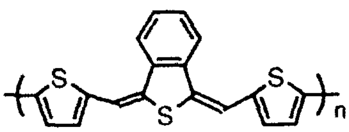
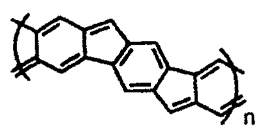




6 a: $R_1 = R_2 = H$ **7**
b: $R_1 = H$; $R_2 = C_{10}H_{21}$
c: $R_1 = R_2 = F$

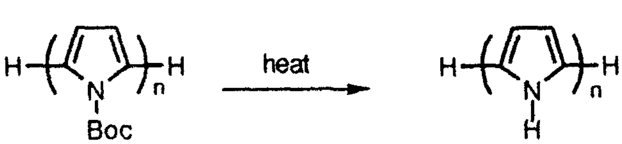
Other interesting low band-gap systems (such as **8**) were reported by M. Hanack (University of Tübingen, FRG) and ladder polymers such as **9** were reported by U. Scherf (Max Planck Institute, FRG). Polymers such as **8** are interesting because they are made up of both aromatic and quinoid rings, while ladder polymers such as **9** are expected to be quite thermally stable.





8 **9**

Motivated by the high stability of conducting complexes of poly(pyrrole) (PPY), S. Martina (Max Planck Institute, FRG) prepared a series of 2,5-pyrrole oligomers and well-defined short-chain poly(2,5-pyrrole) having degrees of polymerization of about 20. Using a Pd-catalyzed coupling reaction between N-*tert*-butoxycarbonyl (Boc)-protected trimethyltin activated pyrrole monomers, soluble N-protected PPY oligomers and polymers (**10**) were obtained. Deprotection was carried out thermally to yield unsubstituted poly(2,5-pyrroles) (**11**) with deprotection yields of 90-95 percent.



10 **11**

ELECTROCHEMISTRY

Electrochemical polymerization and analysis of redox switching was discussed by many groups as facile methods to prepare and study conducting polymers. The Electrochemical Quartz Crystal Microbalance (EQCM) was used in conjunction with spectroscopic ellipsometry by S. Gottesfeld (Los Alamos National Laboratory, U.S.) to study the dependence of film morphology on electropolymerization conditions for the synthesis of PPY and polyaniline (PANI). The reaction of water with the positively charged sites along the backbone, and subsequent formation of poly(hydroxy pyrrole) was postulated to explain the low observed mass increase per unit charge. Most electropolymerizations of pyrrole follow a well-behaved electrochemically-activated step-growth polymerization mechanism, as illustrated by results presented by one of the authors (J.R. Reynolds). Anomalous behavior was observed for pyrrole electropolymerization in aqueous ClO_4^-, BF_4^-, and PF_6^- electrolytes, suggesting the existence of a chain-growth polymerization over part of the film formation.

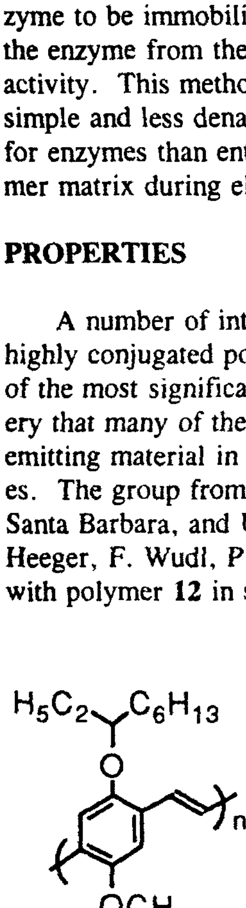
A number of characterization methods have been developed and applied to the in-situ characterization of the electrical and electrochemical switching properties of conducting polymers. Experiments using in situ conductance measurements by J. Kankare (University of Turku, Finland), the EQCM (S. Gottesfeld, Los Alamos National Laboratory, U.S., and J. Reynolds), cyclic spectrovoltammetry (C. Visy, Attila Jozsef University, Hungary), spectroscopic ellipsometry (S. Gottesfeld), and AC impedance spectroscopy (K. West, Denmark) were presented. These results show that electropolymerization conditions, polymer:dopant ion interactions, the electrochemical switching electrolyte, and film morphology all have a strong impact on redox switching.

The entrapment of enzymes in a PPY matrix during electropolymerization is attracting interest as an immobilization technique because it is a simple and rapid method for the generation of biosensors (E.M. Genies, Centre d' Etudes Nucleaires, Grenoble, France). Genies showed that glucose oxidase (GOD) was entrapped in a poly(pyrrole) film during the electropolymerization of a pyrrole solution containing lithium perchlorate

and sodium dodecylsulfate. The GOD/PPY glucose sensor was used in the presence of *p*-benzoquinone as a mediator. The results suggested that the enzymatic reaction occurs only in a layer close to the PPY/solution interface. This led to an alternative approach in which a highly sensitive and stable glucose amperometric sensor was prepared with adsorbed glucose oxidase on an electrodeposited poly(3-methylthiophene) (PMT) film. The high sensitivity and stability of the GOD/PMT electrode are attributed to strong binding forces between GOD and the PMT surface. This strong binding allows large amounts of enzyme to be immobilized, prevents the release of the enzyme from the electrode, and stabilizes its activity. This method seems promising; it is a simple and less denaturing immobilization method for enzymes than entrapment in a conducting polymer matrix during electropolymerization.

PROPERTIES

A number of interesting properties of these highly conjugated polymers was reported on. One of the most significant concerned the recent discovery that many of these polymers can serve as the emitting material in electroluminescent diode devices. The group from the University of California, Santa Barbara, and Uniax Corporation (A.J. Heeger, F. Wudl, P. Smith) reported on their work with polymer **12** in several talks and posters.



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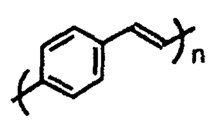

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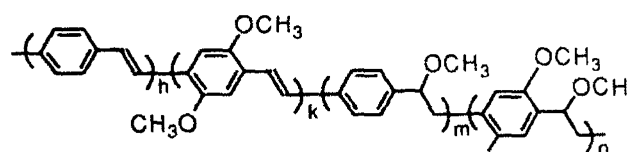
Polymer **12** emits red electroluminescent light and it can be sandwiched between a low work function metal, such as calcium, and polyaniline that has been coated on a polyester (PET) film to provide a flexible light-emitting diode. An LED made up of **12** on an ITO glass plate using Ca and Al and encased in epoxy has been shown to be stable for two months while switching it on and off once a day. In addition, the parent of **12**, namely, poly(phenylene vinylene) (**13**), shows green electroluminescence. The electroluminescence efficiency of these polymeric systems is now comparable to the inorganic electroluminescent systems. The group led by R. Friend (University of Cambridge, England), which discovered the polymer electroluminescence phenomenon, also reported on the electroluminescence of a variety of polymers containing all or some of the groups shown in structure **14** in the form of random copolymers.



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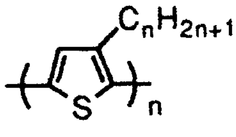
The LEDs are similarly made up of the polymer coated on ITO glass on which is deposited calcium (or sometimes aluminum) and over this can be deposited gold and the device encased in epoxy. By interspersing nonconjugated groups among chains of conjugated repeat units, the Cambridge group has demonstrated that the color (wavelength) of the electroluminescence can be tuned over a range of colors.

Studies of the electroluminescence of poly(3-alkylthiophenes) (**15**) were reported by several groups of investigators from England (University of Cambridge), Japan (Osaka University), and the FRG (Max Planck Institut für Polymerforschung). The color of the emission is reported to be red or red-orange. K. Yoshino (Osaka University, Japan) reported on the blue electroluminescence (l_{max} = 470 nm) of poly(alkylfluorenes) (**16**); G. Grem (Austria) reported on the blue electroluminescence of poly(*p*-phenylene) (**17**).

Attempts to prepare processable polythiophenes, which are more stable in the doped (conducting) state than simple poly(3-alkylthiophenes), were reported by Q. Pei in a collaborative effort among groups in Sweden (Linköping and Chalmers Universities), the U.S. (Uniax Corporation), and Finland (Neste Oy). The idea was to put a lower number of groups on the thiophene



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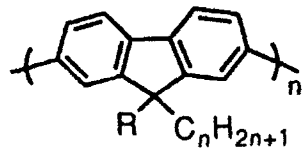

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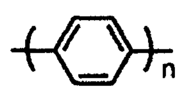

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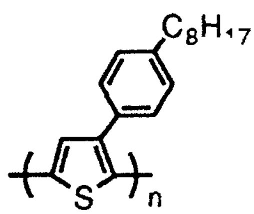
rings, and/or to make the side groups less flexible in order to provide space for the dopant anions. Thus, ferric chloride doped polymers, such as poly[3-(4-octylphenyl)thiophene] (**18**) and copolymers of 3-octylthiophene and 3-methylthiophene (**19**; R = CH_3) or of 3-octyl-thiophene and thiophene (**19**; R = H), show a somewhat greater stability over time than the poly(3-alkylthiophenes) (**15**).



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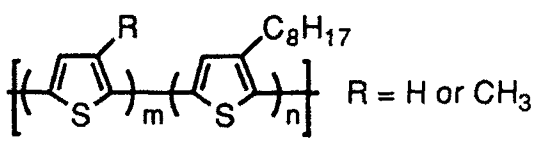

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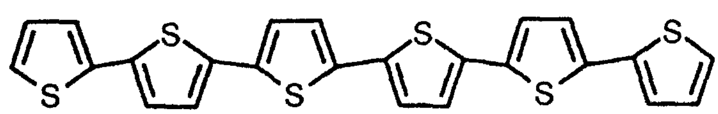
Studies by R.D. McCullough (Carnegie Mellon University, U.S.) on regiochemically well-defined, head-to-tail coupled poly(3-alkylthiophenes) (**15**) have shown that in the ultraviolet (UV) spectrum there are red shifts (longer wavelength) relative to the poly(3-alkylthiophenes) (**15**) made by ferric chloride polymerization of the corresponding monomers, which give greater amounts of head-to-head/tail-to-tail linkages. Thus, for example, λ_{max} for poly(3-dodecylthiophene) (**15**; n = 12) is shifted by about 46 nm in the film, compared to the material prepared by FeCl3 polymerization. This means that the conjugation lengths in this more-ordered polymer are much longer and are now comparable to those in highly ordered very thin films of poly(3-methylthiophene). In addition, conductivity has been markedly increased in these polymers, up to 1000 S cm^{-1}, for the poly(3-dodecylthiophene) doped with iodine.

The work of F. Garnier (CNRS, Thiais, France) has opened up important new ground with regard to organic materials intermediate in size between normal low molecular weight molecules and high molecular weight polymers. Garnier's group has measured the carrier mobility μ_{FET} or a series of thiophene oligomers of which **20** and **21** are representative. A large increase of μ_{FET} with conjugation length has been observed up to the hexamer **20**. Furthermore, for a given chain length, alkyl substitution in the α-position leads to a further rise in mobility, reaching a maximum close to 1 $cm^2\ V^{-1}\ s^{-1}$ for **21.** These remarkable values are attributed to long-range structural ordering in thin films of these "oligomers". The synthesis of even longer oligomers (octamers, decamers) is under way, with the aim of reaching mobilities of the order of 1 $cm^2\ V^{-1}\ s^{-1}$. Garnier stated that



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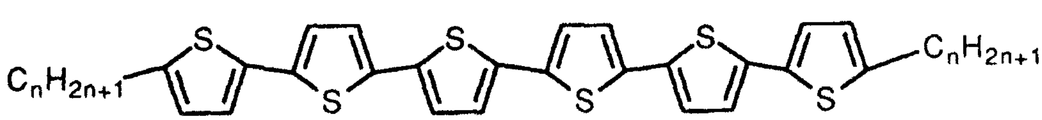

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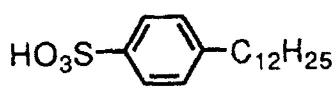
such an accomplishment would make organic-based field effect transistors competitive with inorganic thin film transistors.

APPLICATIONS

A number of interesting new processing results were presented. A.J. Heeger (University of California, Santa Barbara) and coworkers reported on the use of organic sulfonic acids [such as *p*-dodecylbenzenesulfonic acid (**22**) and 10-camphorsulfonic acid (**23**)] to dope polyaniline (PANI). This provides material that is soluble in organic solvents and therefore more readily processable. By co-solution processing, blends may be obtained with conventional polymers to produce fibers, films, etc., having high levels of electrical conductivity and excellent mechanical properties.



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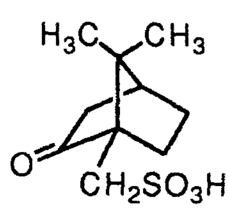

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Blends prepared from PANI doped with anions such as that from **22** have unusual properties. With standard fillers such as carbon, rather high loadings must be introduced to obtain high conductivity. High conductivity is only obtained above the percolation threshold, i.e., the loading level that corresponds to the point at which enough particles touch to form a continuous path throughout the solid [Fig. 1(a)]. In contrast, when PANI is coprocessed with other polymers, a "spider web" morphology of PANI fibers results within the polymeric solid. Thus high conductivities can be effected, even at low doping levels [Fig. 1(b)]. This approach has many practical advantages and was the cause of considerable excitement. As an

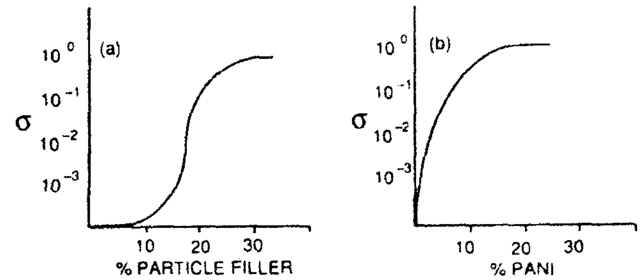


Fig. 1 – Schematic comparison of conductivity vs weight % filler for (a) particles such as carbon, and (b) PANI doped with anion **22**.

example, PANI solubilized with **22** was co-solution processed in decalin with ultra-high molecular weight polyethylene. Fibers with excellent mechanical properties as well as good levels of electrical conductivities were produced. The modulus of the fibers ranged from 80 to 2 GPa and the conductivity from 10^{-6} to 100 S cm^{-1} with increasing concentrations of polyaniline. Also, by using sulfonic acids that are colored as doping agents, the color of the conducting polyaniline (and blends) can be varied.

L. Shacklette (Allied Signal Research and Technology, U.S.) reported that pressed powders of poly(aniline tosylate) possess a superior thermal stability compared to poly(pyrrole tosylate) having a higher continuous use temperature when considering half-lives of about 5 years. *Versicon*™, a dispersible and compoundable form of conducting polyaniline developed jointly by Allied-Signal and Zipperling Kessler and Company (Germany), was blended with thermoplastics by conventional melt processing methods. After blending into poly(vinyl chloride) (PVC), poly(ethylene terephthalate glycol) (PETG), polycaprolactone (PCL), and Nylon 12, the materials were found to follow standard percolation behavior for electrical conductivity. The conductivities were found to be matrix-dependent. Using 10% *Versicon*™ volume fractions, the PCL blend exhibited a conductivity of ~10^0 S cm^{-1} while the PETG blend conductivity was ~10^{-3} S cm^{-1}. Blends in nylon and PVC were shown to be effective as moldable and/or extrudable electromagnetic shielding materials.

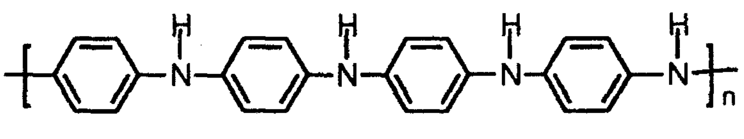
The results reported by A.M. Kenwright from a collaborative effort among researchers at the

University of Durham are pertinent to the above discussion of the commercialization of polyaniline. In the solution spectrum of **24**, the leucoemeraldine base form of PANI, the expected two-line ^{13}C NMR spectrum is observed. However, the solution spectrum of **25**, emeraldine base obtained by reduction of **24**, gave a much more complicated ^{13}C NMR spectrum than anticipated. This observation was explained by postulating restricted rotation about the C-N bonds adjacent to quinoid-imine rings and slow exchange among the many conformers available. In addition, minor peaks were observed in the spectrum of **24**. These were attributed to the presence of about 5% chain defects (including chain ends) created in the oxidative-coupling polymerization reaction by which PANI was prepared.

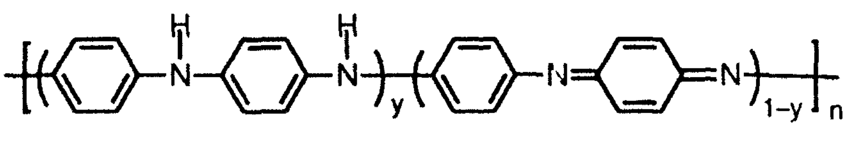
Basic and applied research, which has led to stable, processable, electronically conducting polymers has reached the stage where actual products are entering the marketplace. Thus, electrochemical research has led to the Bridgestone-Sieko commercialization of a polyaniline-based battery in Japan. A number of materials suppliers have committed to the polyaniline area, including Allied Signal's *Versicon*™ noted above. Under the guidance of Dr. Bernard Wessling, Zipperling Kessler & Co., Ahrensburg, FRG, has been aggressively pursuing markets for conducting polymers blended with thermoplastics such as poly(vinyl chloride). He presented details on an interesting electrode application of PANI in an electrostatic speaker produced by a company in The Netherlands. The speaker is "flat" and consists of a thin sandwich of PANI-electroded poly(ethylene terephthalate) (PET) suspended between a set of outer screen-like electrodes. Use of the thin films design permits a very sleek, modern design. This speaker was highlighted in *Stereo* magazine in August 1992.

In a discussion with E. Genies, it was learned that Applications - Chemistry & Technologies (ATC), St. Egreve, France, operates in a different fashion to provide ICPs (intrinsically conducting polymers) to prospective users who do not have the facilities to synthesize "trial" quantities. From this company (managed by Genies), PPY, PANI, and polythiophene can be obtained in quantities suitable for evaluating materials applications.

It was clear from presentations such as that of S. Roth (Max-Planck Institute, FRG), who provided an overview of the current industrial applications of these polymers, that electronically conducting polymers have entered the marketplace in important ways. For example, chips and boards have long been packed in bags made of carbon-filled thermoplastics. As noted above, high loadings of carbon are necessary to effect sufficient conductivity to protect the packaged components from static charge. Once the chip or component is placed in the black, carbon-filled polymer bag it cannot be visually checked. In contrast, thermoplastics, made conducting by blending with an electronically conducting polymer like PANI, protect packaged components against static charge while remaining optically transparent. The latter property allows visual checking of the components for identification numbers or obvious damage. In addition, a number of scientists mentioned that computer monitors are required to have a film that will protect the user against electromagnetic radiation. Again, PANI-thermoplastic polymer blends are believed to be the materials of choice for this application.



24 (PANI: Leucoemeraldine Base)



25 (PANI: Emeraldine Base)

In summary, the International Conference on Science and Technology of Synthetic Metals held in Göteborg highlighted important new basic materials science and growing applications of electronically conducting polymers. It is interesting to note that 15 years ago this meeting was dominated by "charge transfer salt" materials. Over the intervening years, electronically conducting polymers have come to be the dominant theme, but the interesting and useful properties of these materials are leading to a more subtle change in emphasis. The Conference is moving to a broader look at polymers with delocalized electronic states. The novel electronic and optical properties of these polymers from the fundamental point of view offer many opportunities for new and improved materials for the twenty-first century.

Selected Notes on Materials Research from European Laboratories and Workshops

by Joseph H. Magill, Liaison Scientist for Polymeric Materials for the Office of Naval Research European Office. Dr. Magill joined ONR Europe from the University of Pittsburgh, Pennsylvania, where he held Professorships jointly in Materials Science and Engineering and in Chemical and Petroleum Engineering.

KEYWORDS: rigid rod polymers; Buckminsterfullerenes; beamlines; synchrotron facility in Europe; ESRF

COMPRESSIVE STRENGTH IN RIGID ROD POLYMERS

Summary

The First European Tri-service Advanced Materials Workshop was held at Pembroke College, University of Cambridge, United Kingdom, 3-5 September 1992. Various aspects of the properties of rigid rod polymers (RRPs) were addressed by invited speakers from universities and industry. Key issues were considered, and problems, presentations, and discussions centered on liquid-crystalline materials.

We are still "scratching the surface" in our scientific understanding of compressive strength (CS) in polymers. At present, no satisfactory way is known to effectively improve simultaneously the tensile and compressive strengths of RRP. From a mechanics/design point of view, it appears that any modification to improve the CS of RRPs would invariably result in impairment of tensile strength (TS) and vice versa. There always has to be a trade-off. Intermolecular forces appear to control CS in a fundamental sense, since many materials can be ranked according to chemical structure and bonding. The level at which microstructural control can be exercised effectively for an order of magnitude improvement in CS is unknown! It was generally agreed that the microfibril moiety was basic to all RRPs, but the "weak link" that is responsible for the initiation of CS is still uncertain.

Structural defects exist, and most of these can be enumerated, characterized, and observed. Among the most relevant to compressive failure is the kink band, but once it can be detected it is too late to take steps to save the structure! Somehow, the cause or birth of kink initiation needs to be understood in polymers, and it needs to be prevented or avoided well before it becomes visible! The link between microscopic and macroscopic behavior is elusive RRPs. Since the microfibril seems to be the fundamental moiety, we must know how to control and sustain its integrity in the polymer if we are to improve properties. By using mechanics, practical structures can be designed through geometric considerations and calculations. Euler buckling is a well known phenomenon that has been controlled, but not at the microstructural level, to improve polymer properties. It is known

that hollow fibers can resist Euler buckling, but on the solid fibrillar level this is now unimaginable. Even if buckling were suppressed, failure in compression would always result! Interlocking morphological structures that are claimed to be effective in compression appear to be of little use here under tension and dynamic loading. Many related improvements were proposed in the workshop, but all were rejected when scrutinized closely. There was an open question relating to the level of improvement required in Department of Defense (DoD) applications. No definite answers were forthcoming as to whether an improvement should be of the order of $\times 2$, or $\times 10$, or even greater.

Some unique modulus measurement methods are now available. An example is Prof. Robert Young's Raman technique, which is applicable to single fibers for surface and core assessment of materials. Even though this Raman procedure has been used to follow mechanical behavior for the full tension-compression stress/strain for fibers up to failure. the technique still did not provide any new insights as to the origin of kink band nucleation. Many spun fibers have a skin/core morphology that needs to be better understood in relation to compressive failure. Local sample inhomogeneities also influence testing, and these are not always recognized and understood in RRPs. Testing procedures were questioned. A question that should be raised is: Were tests for modulus always made under elastic conditions? Meticulous and generally agreed-upon methodologies must always be followed. Are they?

Theoretical guidelines for compressive moduli and strength are lacking for RRPs. Although computer simulations are now being undertaken by Wierschke and Adams at the Wright-Patterson Laboratories, Dayton, Ohio, for PBT and PBO polymers, only a superficial status report was available for this workshop. Our ability to significantly enhance compressional toughness for RRPs must be further explored and improved. CS values of high tensile modulus/high strength organic fibers are much lower than their metal and ceramic counterparts when fiber reinforcement is used. The reason for the relatively low CS values in RRPs and the means to effect improvements are still moot, despite the considerable effort that has been expended. The writer is tempted to ask—what is the next step?

A POST-BUCKMINISTERFULLERENE VIEW OF THE CHEMISTRY, PHYSICS, AND ASTROPHYSICS OF CARBON — THE ROYAL SOCIETY, LONDON, OCTOBER 1992

Highlights

Shapes have always fascinated mankind. In the 5th century, Democritos stated "There exists only atoms and empty space." The chemistry of benzenoid aromatics probably started in the 1960s, and culminated in the novel and fascinating discovery of the fullerenes (buckeyballs). Fullerenes and isocosahedral virus particles are the underlying geometries applied by Buckminster Fuller in his now well-known geodesic dome architectural designs.

Soot has been around since fire first burned carbonaceous matter on Earth—and so have fullerenes. Carbonaceous fullerene phases are the products of highly evolved stars (that are carbon-rich); they now have been detected, and even isolated, from primitive meteorites. The very exciting science and prospects for fullerenes are only in their infancy, now that some of these polymorphs have been identified analytically and structurally. Different "synthetic" techniques have been followed, but a particularly useful method simply uses a carbon dc arc. From the negative pole and surroundings, diverse fullerenes can be collected.

In general, when carbon is vaporized, fullerenes are produced in varying abundances. Under the most appropriate conditions, controlled by the reaction kinetics and reaction mechanisms (which are far from being well defined), C_{60} can be obtained in yields (up 20 percent); C_{70} and others are obtained in much lesser amounts. Surprisingly, five years ago C_{60} and other fullerenes were known only as ions in a mass spectrometer, now they can be produced in quantity! The spherical molecule C_{60} is unique and the most abundant. Now the chemistry and structure of fullerenes are being vigorously investigated to obtain unambiguous signatures by spectroscopic, analytical, physical, and structural means. Modeling and diffraction analysis are also being pursued.

Reactions between C_{60} molecules have recently shown discrete dimerization; this has been verified by mass spectroscopy. Halogens have been reacted

with C_{60} to give a variety of structures, some of which have been proven. Unfortunately, $C_{60}F_{60}$ is not the "superlubricant" that it was anticipated to be; it is unstable and gives off F_2 on standing. Unlike Teflon it does not have the ability to twist or deform in order to release the strain inherent in the molecule. Mechanisms and products of adduct formation are now being studied. Fullerenes also have a rich reductive chemistry. Doping of C_{60} has been carried out as $C_{60}M_x$, which becomes superconducting at 19 K. The most recent value is 30 K. This metallic behavior is a function of its granularity; its superconductivity per se is said to be fundamentally different from ceramic superconductivity. C_{60} has a sort of π system rolled into a ball and is topologically different from its other allotropes (diamond and graphite); there are mixed orbitals. Fullerenes can be chemically decorated in many ways. They can be substituted so that they have potential value as precursors for polymerization reactions. Photolysis reactions are a recent part of C_{60} chemistry in that C_{60} can be reacted in solution to produce different products that depend on the laser power used.

Optical limiters of C_{60} can be made if precautions are taken to avoid O_2 to prolong the life-time of the molecules; they are transparent at low intensity and opaque at high intensity. Carbon nanotubes have been discovered and collected from the negative pole of a carbon arc furnace. Many of the closed and open needle-like tubules, double and multilayer, have been characterized by electron transmission and diffraction microscopy and have excited much interest in the Japanese semiconductor industry. Potential uses for fullerenes are for batteries, lubricants, semiconductors, etc.

The topological features were addressed in the treatment of the geometries of hypothetical structures derived from a graphite net by inclusion of some other rings as mentioned above. Computer modeling can produce non-positive Gaussian curvature. Polyynes can provide alternate synthetic routes to fullerenes. I was surprised to learn that a flame can be propagated in acetylene without oxygen; this can cause explosive reactions. Work on the synthesis of linear cyanopolyynes in the mid 1970s has been extended, and C_{18}, C_{24}, and C_{30} compounds have been made by decarboxylation reactions, but working in this way with polyynes can be dangerous!

The systematics of the higher fullerenes have been postulated from a set of number rules "leapfrog" and "cylinder" that have been devised to account for all electronically closed π shells with the Huckel approximation. Each particular approach is useful but has its limitations. This theory teaches about geometric pictures, point groups, spectroscopic features, and steric factors. Why can't we make fullerenes from other elements such as boron and silicon?

A High-Brilliance Radiation Source in Grenoble, France

When completed, the European Synchrotron Radiation Facility (ESRF), combined with the nearby High Flux Nuclear Reactor of ILL, will make Grenoble one of the most unique, high-performance scattering research centers in the world. The ESRF facility, with a capability of 5 to 7 GeV, will cover the X-ray region from 0.1 Å wavelengths upward. Structural studies at the atomic and molecular levels will be possible. Applications areas will include microelectronics, superconductors, catalysts, anticorrosion protection agents, earth science studies, submicron lithography, X-ray holography and microscopy, thin coatings and membranes, detection of low levels of localized impurities, glasses, and differential radiography for medical imaging. The full impact of this facility cannot be foreseen. The high flux beamline at ESRF will be available to users in 1994. By the end of 1998, 30 experimental beam lines will be in operation.

Synchrotron and neutron beams are complementary from a scientific problem-solving point of view, hence the selection of the Grenoble facility for the ESRF site. It will truly be a "bright spot" in Europe for materials research in the future. Major areas of study possible in the polymer field include:

- time-resolved small-angle X-ray scattering experiments, down to 0.1 rad, and
- crystallography and diffuse scattering on small specimens (biological and polymeric), with volumes between 1 and 100 μm^3. This requires the collection of the maximum number of reflections from a "single" crystal for the determination of a static structure.[1,2]

Other scientific goals are possible also. The Grenoble facility will have a brilliance about $\times 10^4$ more than the Brookhaven facility, with an estimated beam quality, $\Delta\lambda/\lambda = 10^{-4}$. The quality is determined by the size and brilliance of the X-ray spot. The 65-m beam line is expected to have a resolution up to 20,000 Å.

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Diamond-Related Research, Technology, and Applications in Israel

by James E. Butler, Gas/Surface Dynamics Section, Chemistry Division, Naval Research Laboratory, Washington, D.C.

KEYWORDS: chemical vapor deposition; microwave plasma; diamond-like carbon; ion implantation; laser cutting

INTRODUCTION

Approximately 30 scientists are actively working on the chemical vapor deposition (CVD) of diamond, amorphous carbon, and related topics in various institutions in Israel. The strong interest in increasing both research and development (R&D) efforts in this field was evidenced at many of the institutions I visited (9-15 January 1993) and a 1-day workshop on Diamond Chemical Vapor Deposition that I participated in. In addition to the technical reasons for interest in the science and technological development of diamond CVD, two additional motives were apparent in Israel:

- the generation of new jobs and industries to help assimilate the sizable numbers of new immigrants, and
- the availability of a significant amount of investment resources and loan guarantees to assist the formation of new businesses.

This report is based on a recent trip to Israel during which I visited the Israel Institute of Science (Technion) in Haifa, the Soreq Nuclear Research Center in Yavne, the Weizmann Institute of Science in Rehovot, the Israel Diamond Bourse in Ramat-Gan, Ben Gurion University in Beer-Sheva, and the TEMED industrial park of the NRC-Negev in Dimona. The workshop was sponsored by the Israel Vacuum Society (IVS) and was held at the Weizmann Institute for Science. I summarize the presentations and discussion at the IVS workshop first, then report on the institutions I visited.

WORKSHOP ON DIAMOND CHEMICAL VAPOR DEPOSITION

This workshop was sponsored by the Israel Vacuum Society, Weizmann Institute of Science, Rehovot, Israel, on 13 January 1993. The focus of the meeting was on the current understanding of the deposition process, technology, and the status of the diamond-related efforts in Israel. More than 100 attendees participated. The program included the following talks:

CVD Diamond Growth Mechanisms

J.E. Butler (Naval Research Laboratory, Washington, DC) summarized the gas and surface growth mechanisms of diamond deposition. This talk stressed the role of atomic hydrogen in driving the gaseous reactions, stabilizing the diamond

surface, and the growing in of adsorbed carbon species by hydrogen abstraction reactions. A generic, non-stereospecific model of growth was given that summarizes most of the general parametric variations observed in CVD reactors. This was followed by a stereochemical model for growth from C_1 species on (110) type of surface sites that ties together various other proposed growth mechanisms.

Synthesis of Diamond Films in the Negev

An R&D program (E. Bar-Ziv, KAMAG and Torch, Temed Industrial Park, Dimona) was described that used combustion and dc plasma torches for the growth of thick-film diamond materials. This effort focused on developing a cost-effective way to produce diamond for cutting tools for Israeli manufacturers to help start a new, high tech firm that could provide jobs for some of the new immigrants to Israel. Thermal management and optical windows are also of interest. The combustion flame was used as a low capital method to quickly get up to speed in the CVD diamond infrastructure, while the dc plasma torch is implemented. Precarbonization of the substrates was used as a method to bypass the nucleation induction time on nondiamond substrates. This also gave excellent delamination of films without any transfer of the refractory metal carbide to the diamond film. Laser-induced fluorescence and gas phase Raman scattering are being implemented at the NRC-Negev, which also provides extensive surface and material analysis.

Advances in Microwave CVD Diamond Deposition Reactors

The current state of the art of diamond films growth using microwave reactors was presented (E. Sevillano, D.K. Smith, and R.S. Post, ASTeX, U.S.). Quality exceeding that of type IIa natural diamonds for many properties, growth rates in excess of 4 microns per hour, large deposition areas, and a diverse range of crystalline grain sizes were demonstrated. The next generation of reactors, using high powers and with efficiencies as good as dc arc jets, was discussed. Mass deposition rates of 30 to 60 mg/hr were quoted. Current deposition costs were estimated to be between $100 and $1000 per carat, with an anticipated drop to around $10/carat with the development of a new 75 kW machine.

CVD Diamond Films for Optical Applications

Diamond films of 1 to 40 microns thickness were deposited on 1-in. Si substrates using filament-assisted CVD in a 14-in. evaporator or an ASTeX HPMS 1.5 kW reactor (O. Marcovitch, Z. Klein, and A. Salmon, Rafael, Haifa). The work focused on developing protective optical coatings for IR optical windows. Improvements in the optical smoothness were made by using renucleation/growth cycles similar to that used at NRL and Crystallume to produce smooth, nanocrystalline films.

Deposition of Diamond Films on Cemented Carbides (WC + 6% Co)

Filament-assisted diamond CVD was used to study the nucleation and growth of thin film coatings on sintered tungsten carbide tool inserts (A.K. Mehlmann, A. Fayer, S.F. Dirnfeld, Y. Avygal, A. Hoffman, Technion, Haifa, and R. Porath, Iscar Inc., Maaloth, Israel). Residual film stresses derived from the differences in the thermal expansion coefficients and poor adhesion due to the Co binder were identified as issues. Best nucleation was achieved by using ultrasonication in dense diamond slurries, but the useful lifetime of the slurry was found to be short. Annealing at high temperatures prior to initiation of deposition conditions was found to lower the nucleation density. Adhesion was improved by etching the Co from the samples in atomic hydrogen at high temperatures (>900°C).

Diamond-Like Carbon-Related R&D at Soreq

High density (3.5 gm/cc) amorphous carbon films were deposited by using the high flux MEIRA beam machine at temperatures below 130°C (G.D. Lampert, S. Rotter, Y. Lifshitz, Soreq NRC, Yavne, Israel). A single, symmetric Raman peak at 1550 cm^{-1} was reported for these samples. Typical C ion energies on the sample were 30 to 150 eV. The background pressures were ~ 10^{-6} torr. The samples could be rastered

to cover larger areas. These samples had resistivities in excess of 10^{10} ohm cm, while samples prepared with substrate temperatures in excess of 130°C had densities nearer 2.8 gm/cc and resistivities around 10^6 ohm cm. The high density films were stable up to 700°C. The tribological properties of these DLC films on magnetic recording disks were examined for suitability as wear protective coatings. The results are promising, but the technology is still in the research stage.

Ion Beam Modification of Diamond

An excellent overview of the use of ion implantation to study induced defects, impurity diffusion, and modification of the properties of diamond was given (R. Kalish, Technion, Haifa, Israel). The basic message was that ion bombardment ruins perfectly good diamonds by knocking atoms out of lattice positions, implanting impurity atoms, and generating sufficient damage that the lattice reverts to local sp^2 bonding (graphitization). However, the controlled use of this damage can provide important insights to the properties of the material and modification of the material for technological purposes. The availability of high-quality uniform diamond grown by CVD is viewed as critical to reawaken research into ion implantation into diamond. This field of research has previously been limited to the study of natural stones, which are each unique and of highly variable quality. This has made comparison of different samples difficult. Ion channeling studies can be used to study the quality of homoepitaxial growth, detecting interstitial densities. P-type conductivity can be achieved by the implantation of boron, while n-type has been observed as resulting from damage induced by the implantation of carbon. A revised lattice displacement energy of 37 eV was given (old value, 55 eV). Interstitial carbons were reported to be mobile at room temperature, while temperatures in excess of 650°C were required of vacancy diffusion. Graphite islands induced by the implantation damage also provide for electrical conductivity. The use of diamond as a radiation-hardened material was touted because of the low nuclear transmutation cross-section (3.2 mb vs 80 mb for Si), and the higher energy required to generate electron/hole pairs (13 eV vs 3.6 for Si). Several strategies of using ion implantation to produce near-defect-free doped layers were presented that exploit specific balances between damage and annealing.

Laser Processing of Diamonds

Limited cleavage planes and soft cutting directions in diamond often lead to excess waste or labor in converting a rough stone to a polished, faceted diamond gem. The use of lasers to cut rough diamonds via thermal ablation/burning was presented (Y. Prior, Weizmann Inst. of Sci., Rehovot, Israel). A thorough and straightforward analysis of the optical tailoring of the laser beam focus and the translation/rotation of the stone in 3 dimensions to achieve the desired cut was presented. It demonstrated that the kerf loss in cutting thick stones was competitive with and could even improve on the traditional phosphor-bronze blade. Typical cutting is done with a q-switched, cw Nd/YAG laser operated at a pulse repetition rate of 3 to 10 kHz, 1 to 3 mJ/pulse, 1.06 micron wavelength. The focus of the laser beam (*f* number of the optics) was varied to minimize cutting loss. Cut widths of around 30 microns are typical using *f* numbers between 30 and 60. A unique characteristic of laser cutting is the ability to shape stones into very complex shapes with concave corners (e.g., stars, letters, animals, etc.).

Gem Diamond Cutting

The complex and difficult process of converting a rough diamond into a faceted gemstone was described (A. Caspi, Israel Diamond Institute, Ramat-Gan). The process is divided into:

- marking the rough stone to select the best stone(s) to be cut from the rough;
- dividing, sawing or cleaving the rough;
- shaping or bruting the rough to the shape to be polished;
- polishing the facets; and
- cleaning the stone by boiling in acid and/or laser drilling out defects.

The economics of the trade are such that the diamond cutter has very little markup, so the subtleties of selecting the optimal stone(s) and cutting from the rough are key to his profit and loss. Also

critical are the time and labor spent, and the cutting and polishing losses. In this very traditional trade, the individual markers and cutters are protective of the talents they have learned over the years and are thus reluctant to try new and innovative ideas. However, one of the keys to establishing Israel as a predominant diamond center is the improvements they have made in lowering these marginal production costs by exploiting new technology. In addition to the laser cutting described in the previous lecture, artificial intelligence techniques coupled with TV imaging and multi-axis manipulators are now being used to select the optimal or largest stone available within the outline of the rough stone. These techniques are then used to program the laser to perform the cutting and bruting of the stone in preparation for the polishing of the facets. Israel imports $2.2B in rough and exports $2.7B in product per year. The industry employs ca. 9000 people. The cutting and manufacturing contribute approximately 14 percent of the retail costs, and the profit margins for the manufacturer are only 1-2 percent.

Round Table Discussion: National Priorities

Dr. Bar-Ziv (moderator) began the discussion by asking the general question: "In this field where overseas efforts are well advanced, and in the context of a nation of limited size and resources, high immigrant flux, and strong technological base, should the national priorities be directed at research, production and development, or applications?" He pointed out that 1 to 3 small companies are presently active in CVD diamond research and the $300M Israeli cutting tool industry could easily and willingly consume locally produced CVD diamond tools up to 10 or 20 percent of their market, or $30 to $60M. In addition, loan guarantees totaling $2B are available from the government to support new companies and ventures that can provide new Israeli jobs.

Dr. Wolff (Ministry of Science and Technology) stated that the role of his office was to support the research phase of a field that is directly connected to development and application of a technology. They particularly like cooperative programs between academic, national laboratories, and industry. Investment in research is seen to be critical to maintaining a leading tecl...ical edge in industry. He saw the need to develop an infrastructure to apply the technology locally, even if it is not leading the international efforts. He also pointed out that limited funds are available and the competition for them is primarily on the basis of scientific excellence.

Dr. Geffen (Ministry of Defense) stated that the Ministry of Defense had definite needs for diamond technology in the area of optical windows, particularly free-standing ones for IR sensors. He has supported the NRC-Negev and Raphael over the past 2 years and sees the shape, quality, and polishing of CVD diamond materials as key issues of the future

Dr. Goldshmidt (Ministry of Industry and Commerce) noted the interest demonstrated by the packed house at this workshop with ca. 15 percent of the participants from industry. The Ministry of Industry and Commerce was looking primarily for projects that impact jobs and commerce, not infrastructure. The Ministry is willing to match industry investment 1 for 1, or possibly 2 to 1. He pointed out that there is several hundred million dollars of venture capital currently looking for investments. He recognized that while it was difficult to get two Israelis to agree and collaborate on anything, that exceptions such as the high T_c superconductivity consortium exist in the technological fields. Could this be done in the field of CVD diamond technology?

Dr. Shlomo Rotter (SOREQ) pointed out that CVD diamond was far ahead of high T_c superconductors in commercial development and application.

Professor Rafi Kalish (Technion) attacked this emphasis on "applied" science, saying that there was a major problem in that it is often perceived as *too applied* by the academics and *not applied enough* by industry. He requested that the ministries define what they mean by "priority" and develop programs to bridge this gap between academe and industry. Professor Kalish gave several examples of Israeli scientific innovations that had withered on the vine and were plucked by overseas concerns. Doctor Wolff responded by saying that they were supporting "applied" research and that they see the need to do more to bridge the gap.

R. Porath of ISCAR, a cutting tool manufacturer, suggested that the focus should be on new CVD diamond technologies, not the current ones in

which Israel is already 5 years behind. He would like to see investment in basic research to develop new diamond CVD systems.

SUMMARIES OF VISITS TO SPECIFIC INSTITUTIONS

Israel Institute of Science (Technion, Haifa, Israel)

My host was Prof. Rafi Kalish, Solid State Science Institute. I also visited with Prof. Azra Ron, current head of the Institute, and Alon Hoffman, newly appointed Lecturer (Assistant Professor) in surface science. Professor Kalish is one of the leading researchers in the world on the use of ion implantation for doping and modifying semiconductors, and is particularly experienced with diamond technologies. He has a new student who is very interested in doping diamond for n-type conductivity, probably with Li. It is likely they will try several strategies:

- heavy implanting and annealing, followed by etching the top, heavily damaged (graphitic) layer away—leaving a regrown, lightly doped layer;
- putting a solid Li source in the CVD growth chamber (hoping for solid-vapor-solid transport); and
- implanting with low dose into hot crystal so that damage anneals out as it occurs.

They currently have an operating filament-assisted diamond CVD chamber (set up by Y. Avyigal). They have ordered the components for a microwave plasma system and expect to set it up in the near future. Alon Hoffman has planned temperature-programmed desorption, AFM, and STM on natural diamond (100), (110), and (111) surfaces. He is currently looking for the funding for the AFM/STM. Joe Zahavi, director of the Israel Institute of Metals at Technion, is active in the use of laser sputtering/ablation for depositing amorphous carbon films, and is close to purchasing a microwave plasma diamond deposition system.

Soreq Nuclear Research Center, Yavne

The main effort here is on a high flux C ion beam deposition system (MEIRA). This impressive machine is capable of isotope separation using a high flux (100 microamp, as I recall) magnetic sector, 50 keV, which can then be focused and decelerated to 10 to 300 eV on sample. The sample can be rastered and is usually at low (room temperature to several hundred °C) temperatures. The source is a sophisticated curved graphite slit with a CO_2 plasma behind it. This machine is used for both oxygen atom erosion studies and amorphous carbon film deposition. Also available was an ion beam-assisted deposition (IBAD) system with a small Kaufmann Ion Source. This site is small, total ca. 200 scientists; my host was Dr. Y. (Shi) Lifshitz. The researchers here seemed to be very interested in finding applications for their existing ion beam machine. Management is definitely examining arguments for setting up a focused diamond effort and is particularly concerned about having a definite application/consumer identified before committing significant resources. Another group working on electro-thermal plasma (ETP) sources was interested in trying these out for diamond CVD. Electro-thermal plasma is an ablative plasma in polyethylene, injected into a water gel, and driven by a pulse-shaped capacitive power source. The electrical pulse shaping is used to tailor the impulse profile for driving projectiles. Although this very high temperature thermal plasma source could produce the active radical species, its pulsed nature will make maintaining the appropriate surface temperature difficult for the deposition of coatings.

Weizmann Institute of Science, Rehovot

Professor Y. Prior has established a state-of-the-art laser physics laboratory for studying nonlinear phenomena and materials, principally, for wave-mixing phenomena. His involvement in diamond comes from the development of laser sawing of diamond. This was funded by the Israel Diamond Institute (a research organization supporting technological developments for the significant

diamond gem industry in Israel, imports of ca. \$2.2B and exports \$2.7B, which account for approximately 30 percent of the worlds' cut gem market). Laser sawing machines developed by Prof. Prior are currently used for sawing and bruting stones where normal sawing methods would yield smaller stones and larger loss. In principle, the laser method can beat normal methods in terms of the loss of rough (kerf loss), but it is capital- intensive and too modern for a very traditional industry. Professor Reshef Tenne of the Department of Materials and Interfaces, Weizmann Institute, and president of the Israel Vacuum Society, has done some nice work on analogs to the fullerene chemistries with tungsten and molybdenum disulfides. He showed me electron micrographs of the onion-like structure of spheroids and rods.

TEMED Industrial Park of the Nuclear Research Center of the Negev (Dimona)

Doctor Ezra Bar-Ziv hosted my visit at the industrial park adjacent to the NRCN. Staff scientists from the NRCN (ca. 30) were bussed over to attend my seminar. A definite interest in surface science and fundamental mechanisms of diamond CVD was shown. The discussions indicated that they have state-of-the-art analytical and surface science facilities at the NRCN. The combustion flame diamond deposition of Bar Ziv's group is done at NRCN (as well as the nucleation and diffusion barrier studies) so I was unable to see this work.

Torch TEMED, a new (10-month-old) company in the industrial park, is a spin-off of the NRCN. It has set up a dc plasma torch system (60 kW) for growing thick-film material for the Israeli tool manufacturing industry and possibly, thermal management applications. The staff of this company is drawn from the recent immigrant pool (Russian) and are led by an excellent and motivated physicist. The torch system is simple and functional. It was set up in less than 4 months. Many things were home-made but adequate to the job. Ingenuity and the understanding to do a safe job were evident.

The TEMED Industrial Park is one of several set up adjacent to the major scientific laboratories and academic institutions in Israel. It is built around an "incubator" association. This is the principal catalyst for the development of new startup companies, and provides the space, support services, marketing, investors, and venture capital for the first 2 years in the development of businesses based on advanced technologies. The main fields of activity at TEMED are: Optronics (Lasers), Chemistry, Energy, Electronics, Medical Instrumentation, Ecology and Environment, Detection and Identification devices, Biology, and Applied Mathematics and Advanced Computation. They currently have 15 projects active that employ 80 scientists and engineers.

Ben Gurion University, Beer-Sheva

At the Ben Gurion University, Prof. E. Bar-Ziv (Department of Mechanical Engineering) studies the combustion kinetics of solid particles by using electro-dynamic suspension of a single particle in reactive gas flow. The particle is actively stabilized at a fixed point in the flow by using its shadow projected onto a linear diode array. The particle can be heated with a cw infrared CO laser, and temperature controlled by using two-color IR pyrometry. The kinetics of reaction are followed by a video camera to record the changes in particle size and shape, and the electrodynamic suspension system to infer the mass of the particle. He is considering using this apparatus to study the kinetics of suspended diamond particles.

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Computer Science

Eurographics '92

by Lawrence J. Rosenblum, Liaison Scientist for Computer Science at the Office of Naval Research European Office. He is on leave from the Naval Research Laboratory, Washington, D.C.

KEYWORDS: computer graphics, scientific visualization, multimedia, human computer interface

INTRODUCTION

"A picture is worth a thousand words" goes the old saying. Well, now it's worth a million numbers! From scientific visualization methods that represent the outputs of complex numerical simulations on supercomputers, through the use of virtual reality to create new visual methods for concurrent engineering (product design), and new multimedia displays and animations for training, we have become increasingly dependent on computer graphics.

To understand these numbers, consider that one million data points is a single time step (i.e., one picture) in a three-dimensional simulation that is only 100 data points in each dimension. The same remark holds for a 10-second animation at 10 frames/second covering a 100 × 100 pixel region of the screen in a multimedia display. Computer graphics research holds the key to unlocking doors to the many technologies that are emerging in the 1990s, based on the use of visual perception to gain understanding.

Eurographics '92, the annual conference of Eurographics—the European Association for Computer Graphics—was held in Cambridge, U.K., on 9-11 September 1992, with workshops and tutorials held earlier. Nearly 400 attendees came from 25 countries, including about a dozen from Japan and 30 from the U.S. The relatively small attendance (contrasted with the SIGGRAPH Conference in the U.S.) is attributable to the activities of country-wide European computer graphics associations. These apparently serve the needs of many practitioners, so that Eurographics attracts leaders within each country.

The conference had three plenary sessions with invited speakers. The remaining sessions had three parallel tracks—usually two paper tracks and one STAR (STate of the ARt) track. Conference paper sessions included Multimedia, Animation, User Interfaces, Visualization, Radiosity, Rendering, Fundamentals, Algorithms, Modeling, Curves and Surfaces, and Applications. The STAR tracks had 1 or 2 speakers talk on a focused topic of current interest. Forced to make choices, I emphasized visualization, multimedia, and applications while attending several STAR report lectures.

The welcome address was given by Bob Bishop, managing director of CADCenter Ltd., Cambridge, U.K. He overviewed the impressively large number of graphics companies that have arisen in Cambridge and that maintain close ties with the university. Particular areas of expertise

in Cambridge are CAD/Solid Modeling, HCI (human/computer interface technology), and GIS (geographical information systems).

PLENARY ADDRESSES

There is little doubt that computers will invade our lives in almost unnoticed, pervasive ways. Those of us in the scientific R&D world spend little time contemplating these issues; we are more concerned with how computers can be used to do science, improve manufacturing, develop specific end products, etc.

Mik Lamming of Xerox EuroPARC, the invited speaker for the opening session, is investigating this issue. He described work at EuroPARC, which numbers some 30 people about equally divided between cognitive, social, and computer science. They look 5-10 years out on the horizon (10 seemed a better estimate than 5 after hearing the talk), seeking to understand technology and how it will work in practice. The focus is on the development of "everyday" technology. Lamming noted that word processing, perhaps the most utilized applications software today, is used by only a small segment of the population. On the other hand, everyone uses microprocessor-driven appliances. Lamming predicted that these microprocessors will collaborate and cooperate with each other. A sample application would be a home that operates semi-automatically based on the owner's behavioral patterns. He predicted that video and other technologies will track individual movements, not only in the home but also in the workplace and elsewhere. Time differences between frames will be the basis of the storage mechanism. The computer we will all wear for this purpose must be compact—say wristwatch-sized. The device must have a low cognitive load. Lamming also noted the potential military benefit of a technology that automatically determines everyone's location and movements.

While Lamming spoke of the benefits of such technology, many in the audience worried about the "big brother" aspect. Certainly, the potential for abuse is high. In concluding, Lamming appealed to the data visualization community to add the visualization of personal data to its list of research topics!

The need for such studies, especially when the human/computer interface (HCI) is involved, is illustrated by a story from Tom Hewett's (Drexel University) plenary address on perception and HCI. He told of a human factors person touring a nuclear power plant. A light on the power console was blinking red, but his hosts did not appear concerned. Not wanting to make a scene, he moseyed up to the light. Written on a note that was taped above the light was EVERYTHING IS NORMAL WHEN THIS LIGHT IS BLINKING RED!

MULTIMEDIA

Multimedia is a booming business, and presenters in this session gave several approaches and applications. An unusual multimedia system was described in "Visual Composition and Multimedia," by Vicki de Mey et al. (University of Geneva). The system, oriented for developers rather than end users and written in C++, uses a technique they call visual composition to create and interact with multimedia applications. An internal graph representation is used with classes Node, ConnectionPoint, and Edge. Data flow is through defined subclasses of these classes, and graph class hierarchies can be created. The authors note the similarity of this approach to scientific visualization systems such as AVS (Advanced Visualization System) that allow construction of powerful networks by linking modules in defined ways.

They illustrated the multimedia system with an example called a virtual museum. Although not virtual in the sense of immersing the user within the scene, the museum was a 3-D building with both 2-D and 3-D artifacts, plus sound. The user could walk through the scene and manipulate objects by using techniques familiar to multimedia users. One could visualize an eventual merger between virtual worlds and multimedia. Research issues involved in developing the system include real-time response and user feedback, handling multiple data streams, developing special-purpose hardware, and concurrent usage.

A more standard multimedia system, from a user's viewpoint, was given in "Pandora: An Experiment in Distributed Multimedia," by T. King (Olivetti Research Limited, Cambridge, U.K.).

The paper describes the Pandora workstation, 19 of which have been deployed at Olivetti and at the Cambridge University Laboratory. Its distributed applications include video mail, video conferencing, and real-time media delivery services. The system uses the capabilities of a UNIX host, but it uses a specialized processing box for high-bandwidth, time-critical, and device-dependent processing. Data communication is over a 50 Mbit/second ATM (asynchronous transmission mode) network. A Transputer is used as the process controller. The author's note, however, that the advent of higher speed busses and processors will probably alter their fundamental approach; they foresee processing pixels and sound samples directly rather than through rigid interfaces, as is currently done. Still, multimedia has arrived. Video and sound are effectively integrated with hypertext, creating new capabilities both in publishing and for interacting with colleagues.

SCIENTIFIC VISUALIZATION AND APPLICATIONS

Data visualization papers appeared in both in the Visualization and Applications sessions. Three of the more interesting papers are described here. The first examines the visualization pipeline as it exists in the many commercial systems that are destined in the 1990s to become as commonplace on scientists' desks as their word processors. It suggests methods to enhance user interaction and data flow. The second deals with volume visualization, perhaps the key visualization algorithmic breakthrough of the past decade. The ability to display objects without constructing surfaces has evolved from the medical imaging community. It has proven to be important in achieving scientific understanding in numerous disciplines. The process is not yet real-time, but both algorithmic and hardware research are moving toward achieving this goal. Underwater imaging is but one of many fields of naval interest where this research is finding applications. The third paper demonstrates how research in photorealistic rendering algorithms produces cost savings in manufacturing prototyping.

In "The Visualization Input Pipeline," W. Fegler and F. Schroder (FhG-IDG, Germany) argue that the classic visualization pipeline should be extended into an output pipeline (that contains most of the commonly used pipeline) and an input pipeline for semantical interaction. They note that today's application builder systems (AVS, apE, IRIS Explorer, Data Explorer, etc.) are primarily output-oriented. They argue that a dual system, where each output operation has a corresponding inverse input operation, will allow for better user interaction through data probing as well as being direct ports back into the data visualization process. Several architectures are proposed for achieving this result.

Improving the speed of volume rendering is an important research area because of the growing use of these methods in scientific data visualization. In "Template-Based Volume Rendering," Roni Yagel (Ohio State University) and Arie Kaufman (SUNY Stony Brook) observe that a ray cast from the image plane will yield a template that can be used to reduce processing requirements. Attempting this approach from the image plane leads to view-dependent sampling difficulties. However, the template can be used effectively by casting rays from a base plane parallel to a face of the volume. All rays no longer need be processed; it is enough to process one ray, store the results, and generate subsequent rays by using this stored template. One must then transform from the base plane to the image plane. This, however, is a 2-D image transformation that is simpler to solve than the original 3-D problem.

A particularly enjoyable paper was "A CAD System for Color Design of a Car," by T. Oshima (Toyota Motor Corp.) et al. The paper reports on more than a half-decade of effort to produce photorealistic renderings of an automobile for paint selection. The system uses physical-based modeling of light to obtain accurate reflection data for different sky lighting and weather conditions and a variety of paint types. It uses analysis of the CRT colorimetric characteristics to maintain consistency and accuracy. Parallel computing provides high-speed computation in support of interaction. Daniel Whitney (previously at ONR European Office) saw this work in progress at Toyota during a tour of duty at ONR-Tokyo about a year ago. It impressed him from the manufacturing viewpoint. The system had developed such that it was replacing paint prototyping by using clay models. I was pleased, however, just to see an application that

truly justified the attention paid by the computer graphics research community to *n*-th order lighting effects!

CONCLUSIONS

Because Eurographics covers all of computer graphics, it lends itself to the extraction of broad-based conclusions about trends in European computer graphics research, rather than focused research issues.

The emphasis on multimedia at Eurographics '92 reflects a general European thrust. The large European research program ESPRIT has made multimedia solutions for consumer, professional, and business applications the focus of one of its seven funding areas (Advanced Business and Home Systems - Peripherals). Discussions with European colleagues have indicated that several universities are expanding their staff to establish multimedia groups within their departments.

The lack of virtual reality research papers was surprising, although several European companies were represented in the exhibition. There are European start-ups in virtual reality as well as a few older, ongoing research programs. The latter appear to have arisen largely outside the computer graphics community (from the aerospace and artificial intelligence communities, in particular), while many of the newer start-ups are taking place within. These groups do not appear to have much communication, nor has any one European conference for virtual reality research arisen. ONR Europe is sponsoring a virtual reality workshop in conjunction with Eurographics '93 in Barcelona this September.

Scientific visualization had world-wide representation, although the number of papers was quite probably limited by the timing of the IEEE Visualization conference (held in October) that tends to be well attended by leading European practitioners. Europe's leaders meet at a separate Eurographics Scientific Visualization Workshop every April.

Some topics from this conference that I did not cover are areas of European strength. One example is geometric modeling (curves and surfaces) where European activities have recently been described in G. Neilson's report "Mathematical Modeling and Representing Objects in 3-D Space—Freeform Curves and Surfaces '92" [*ESNIB* **93-03**, 169-174 (1993)]

PROCEEDINGS AND STAR REPORTS

The conference papers have been published as a special issue of *Computer Graphics Forum*, the international journal of the Eurographics Association (Vol. II, No. 3). The STAR reports are published by Eurographics as *EG92 SA*, Eurographics Technical Report Series ISSN 1017-4656.

Environmental Science

Changes in Fluxes in Estuaries: Implications from Science to Policy

by Cynthia J. Decker, Environmental Quality Liaison, Office of Naval Research, Ocean Sciences, Arlington, VA.

KEYWORDS: algal blooms; ecosystem management; nutrients; anthropogenic influences; toxicants

INTRODUCTION

A joint meeting of the U.S.-based Estuarine Research Federation (ERF) and the United Kingdom (U.K.)-based Estuarine and Coastal Sciences Association (ECSA) was held 13-18 September 1992 at the University of Plymouth (formerly the Polytechnic South West), Plymouth, U.K. This was the first time that the two organizations met together.

The ERF is an 18-year old group that serves as an umbrella organization for a number of regional estuarine societies, each of which has its own annual meetings in addition to the national meeting held once every two years. The ECSA is roughly the same age and, although it was originally organized in the U.K., it has now expanded its charter to include international membership.

The two organizations have had intellectual ties for a number of years, but this meeting was the first attempt to actually bring together the members of both groups to exchange information and opinions about coastal and estuarine science and the application of this science to ecosystem management.

Four plenary lectures were presented. Contributed papers were divided into a number of sessions, including fluxes and residence times, particle-chemical interactions, estuarine eutrophication, microbial transformations, response to toxicants, storm events, larval recruitment, tropical systems, response of fisheries to changing fluxes, estuarine management, changes in river inputs, estuarine processes, estuarine modelling, the Columbia River Estuary, and special programs. Many of these sessions overlapped in their ideas; some of the highlights and basic issues are reviewed (all references are to unpublished abstracts from the meeting).

The current research on estuarine systems presented at these meetings is of particular relevance to the Office of Naval Research (ONR) because of the increasing emphasis within the Department of the Navy on shallow, coastal systems. In addition, the ways in which Navy shore and ship activities in home and foreign ports may cause changes in the biological, chemical, geological, and physical functions of ecosystems is the focus of regulations imposed on the Navy by other agencies and governments. As a result, there is rising concern in the Navy for the potential impacts of their harbor operations on natural systems.

ISSUES

The primary theme of these meetings was mass fluxes in estuaries and the impact of human activities on these fluxes. Most of the presentations dealt with variations in natural processes affected directly or indirectly by human populations. Anthropogenic impacts on estuaries were discussed primarily in terms of additions of toxic substances or excess nutrients (nitrogen and phosphorus, primarily) to these systems. Other issues of particular interest included the effects of physical changes in the estuary on natural communities and the ways in which cooperation between scientists and policymakers can lead to development of sound alternative resource management practices.

Toxic Substances

Most of the papers that examined contamination by toxic chemicals were descriptive. These studies characterized the concentrations in estuaries on various scales and in various media (water, sediment). Additionally, some studies examined the sources of the contaminants (land, atmosphere, rivers); others included the concentrations in some organisms (fish, primarily) and attempted to infer, through correlation analysis, some relationship between tissue levels and observed water and sediment concentrations.

Very little research was presented that examined the mechanisms by which these toxicants may be impacting the estuary. For example, the studies that did measure levels of toxicants in organisms did not then determine the means by which the concentrations in the water and/or sediment may have led to (or if they do, in fact, lead to) high concentrations (of fin rot, lesions, tumors) in the animals. These kinds of correlation studies have been done for years, and it was disappointing to see more of the same. Unfortunately, very little research on bioavailability of toxicants or on population or community responses in situ to single or, especially, multiple toxicants is being done anywhere. These studies are critical for estuarine managers; they need to understand when toxic chemicals in marine environments are truly causing irreparable ecosystem damage. They need to know when and at what concentrations these toxicants must be regulated and remediated and when it is not necessary to take drastic and expensive measures to eliminate them.

Exciting information on sources of toxic substances was provided by Dr. Hans Klamer (Rijkswaterstaat, Haren, The Netherlands) who has found, through analysis of a variety of existing data, that the primary source of PCBs to the North

Sea is the atmosphere, both wet and dryfall. The primary source of the aerosols is smokestack emissions.

Nutrients

Results presented on studies involving excess nutrients in estuarine environments were much more interesting than those on toxic inputs. In general, these papers examined the mechanisms by which large increases in nutrient loading can lead to algae blooms and then to conditions of extremely low or no oxygen in a system.

There has been a lot of research in the past few years on the ways by which excess nutrients (usually added as sewage effluent or agricultural runoff) affect estuarine ecosystems. An excellent summary of the changes in nutrient inputs to a system over time was presented by Dr. Scott Nixon (University of Rhode Island, U.S.) who presented historical data on Narragansett Bay, RI, from the 1600s to the present. His emphasis was on the changes in technology and land use that have drastically increased nutrient loadings to the Bay in the last 150-200 years. This situation has generally been the case for most estuaries in the U.S. and the U.K. Dr. Nixon's talk provided an overview of the conditions that may have led to eutrophication (the process, natural or not, by which an aquatic system becomes enriched in nutrients) problems in many of these systems. He concluded by discussing the results of recent research in Narragansett Bay that has traced the evolution of eutrophic conditions over the course of seasons and the results of experiments that have elucidated the means by which this occurs.

Increased nutrient loadings do not universally lead to eutrophication and very low (hypoxia) or no oxygen (anoxia) in bottom water and sediment, however. Talks by Dr. Jonathan Sharp (University of Delaware, U.S.) and Dr. J.R. Pennock (University of Alabama, U.S.) on conditions in Delaware Bay showed that nutrient (nitrogen and phosphorus) loadings to that estuary are very high and have persisted in spite of some efforts to reduce them through treatment of sewage. No algal blooms or hypoxic conditions have been seen in bottom water or sediment, however. This is the result of strong physical turbulence, which keeps the water column vertically mixed throughout most of the year, and high turbidity (due to sediment resuspended by the physical turbulence), which limits the phytoplankton growth.

This system is in contrast to Mobile Bay, Alabama, where the nutrient concentrations are only moderately high and yet they have apparently caused summer hypoxic events. In the case of Delaware Bay, the scientific facts have led to the recommendation from scientists to regional managers that expensive conversion to tertiary treatment of the sewage treatment plants for removal of excess nutrients may not be necessary; it is possible that management of non-point sources will be sufficient to keep the biogeochemical oxygen demand (BOD, the extent to which geochemical and biological processes use oxygen; high BOD results in hypoxia or anoxia) at acceptable levels. This is quite different from management conclusions reached with regard to western Long Island Sound where large inputs of secondarily treated sewage effluent may have promoted the algae blooms that led to severe anoxic events in those waters in the late 1980s.

These studies have shown that all systems do not respond to a pollutant input in the same way or with equal magnitude. The natural variation among estuarine systems may require different management plans among them. In addition, the Delaware Bay study has shown that scientists and managers can work together to develop scientifically sound management decisions.

Another excellent talk was given by Dr. Hans Paerl (University of North Carolina at Chapel Hill, U.S.) who discussed the nutrient contribution to estuaries from the atmosphere. The absolute contribution from both wet and dryfall is much greater than previously thought and may become relatively greater as riverine and non-point sources of nitrogen and phosphorus are reduced. In fact, Dr. Paerl has concluded that algal blooms and eutrophication in estuarine and coastal waters that apparently have no large riverine and non-point sources may be the result of these large, previously unsuspected atmospheric inputs.

As mentioned before, the results from studies on toxic substances have generally been less useful to environmental managers than those on excess nutrients. It may be that this arises from a fundamental difference between the ways in which these two topics have been approached. The work on

excess nutrients came about through the identification of a problem in estuarine systems—low or no dissolved oxygen in bottom water and sediment during certain times of the year, causing massive kills of some species of fish and benthic invertebrates. Research into the causes of this situation led to the understanding of the interaction between the growth of phytoplankton, the grazing communities in the water column, the biological oxygen demand in the estuary, and, finally, the effect of high nutrient loadings.

Many chemical pollutants, on the other hand, have been identified as being toxic primarily in the laboratory. The actual effects of these substances on estuarine organisms, in situ, much less on populations and whole communities, has yet to be determined. In other words, toxic chemicals are estuarine pollutants that have yet to be identified with a specific problem. They are suspected to be the root cause of everything from declines in commercial shellfish and finfish populations, to losses in benthic diversity, to increases in the occurrence of disease and cancer in marine organisms. Their real role(s) in natural marine ecosystems has yet to be determined.

Physical Changes

In addition to toxicants and nutrients, humans have also caused changes in estuaries through physical manipulation of these systems. An excellent example of the results of such manipulation was provided in one of the plenary sessions by Prof. Piet Nienhuis (Netherlands Institute of Ecology, Yerseke, The Netherlands). Professor Nienhuis discussed the changes (physical, chemical, and biological) that have occurred in the Oosterschelde. This estuary has experienced reduced oceanic mixing as the result of the placement of a partial tidal barrier across its mouth, and reduced freshwater input because of dams upstream on its river. An obvious change in response to the construction of the barrier and the dams was a switch in the aquatic fauna from communities typical of turbulent, well-mixed estuaries to those species more commonly seen in relatively quiescent tidal lagoons.

Examples of changes in estuarine systems as a result of physical barriers to freshwater input were provided in two papers from South Africa (J.H. Slinger, S. Taljaard, CSIR, Stellenbosch, South Africa, and J.L. Largier, Scripps Institute of Oceanography, La Jolla, CA; and A.K. Whitfield, J.L.B. Smith Institute of Ichthyology, Grahamstown, South Africa, and T.H. Wooldridge, University of Port Elizabeth, South Africa). These papers summarized the effects of upstream dams on bar-built estuaries in southern Africa. The most obvious effects were the increases in salinity and temperature that occurred as direct physical results of decreased amounts of fresh water. The change in seasonal flow regimes (i.e., flood events) led to a build-up in nutrients and toxicants, having all of the effects of those materials, as discussed previously. Changes in the faunal communities over time eventually resulted from such physical and chemical manipulations. These papers clearly show that the chemical and biological cycles of most estuaries are dependent on the hydrodynamics of the system, which have proven to be increasingly vulnerable to alteration.

Management Alternatives from Science

Another major topic at these meetings was the connection between scientific research and environmental management. In several sessions, the results of cooperative efforts between government and academic scientists were presented. Frequently, factual information or critical interpretation of the data available is provided by scientists. This provides a sound basis on which management decisions can be made. The Delaware Bay project discussed by Dr. Jonathan Sharp, summarized previously here, exemplifies this type of cooperation.

Another excellent talk addressing this issue was that of Dr. Jeffrey Levinton (State University of New York at Stony Brook, U.S.). His presentation concerned the various spatial and biological scales by which natural systems are affected by anthropogenic influences. He used as an example a cove on the Hudson River contaminated with the heavy metal, cadmium. Organisms within the cove take up cadmium in feeding but have adapted to those concentrations over time, meaning the benthic communities there are similar to those in uncontaminated coves. On this scale, perhaps a management decision to clean the cove is not necessary. On a larger scale, however, the situation is different. A large export of particulate

cadmium out of the cove into the Hudson River reacts with salt water farther downstream, causing the release of the dissolved form of the metal; this is taken up by blue crabs, among other organisms. On this scale, there is, in fact, a need for the cove to be cleaned up. Pollution problems need to be scientifically assessed at a variety of spatial-biological scales so that sound decisions about the best and most cost-effective means of managing the resources can be made.

In addition to the issue of scaling addressed by Dr. Levinton, the development of appropriate criteria for assessing the health of a system was dealt with in several other talks. The papers from South Africa on the effects of dams on estuarine flow (cited and discussed in the section on Physical Changes) provided the example of how the management of the Wolwedans Dam on the Great Brak estuary was modified to provide the system with the freshwater floods required for the health of the system. Prior to this decision, the major "criteria" for the construction of dams was the need for freshwater by the human populations upstream of the estuary.

A paper on the Chesapeake Bay by R.J. Orth and K.A. Moore (College of William and Mary, Gloucester Point, MD), W.C. Dennison and J.C. Stevenson (University of Maryland), V. Carter (U.S. Geological Survey, Reston, VA), and P.W. Bergstrom and R.A. Batiuk (U.S. Environmental Protection Agency, Annapolis, MD) also addressed the issue of revised water quality criteria. They base their revisions on studies of the submerged aquatic vegetation (SAV) species, abundance and distribution throughout this estuarine system, and how these have decreased in the last decades as a result of increasingly poor water quality. Based on the changes in SAV, they feel that current water quality criteria are not adequately meeting the needs for the health of the ecosystem. They propose criteria based on the chemical parameters important for the health of SAV. The new criteria would include measurements of the light attenuation coefficient, chlorophyll a (a measure of phytoplankton standing stock), total suspended solids, dissolved inorganic nitrogen, and dissolved inorganic phosphorus. The variations in these parameters would enable managers of the Chesapeake system to determine when water quality is deteriorating in an area where SAV still remains and take action to reverse the trend. In addition, these measurements would tell managers when the water in an area from which the SAV has disappeared has improved to the point that restoration efforts could be attempted.

The key to the development of all of these alternative scientific criteria is a change in the attitude on the part of environmental managers that the only relevant standards for the health of an ecosystem are based on human health concerns. In the case of the South African estuaries, the notion that fresh water flowing into the sea is wasted has been overturned in favor of the idea that the natural flow regime is important to preserve the natural non-human communities and that these communities are as important as the human ones requiring fresh water upstream. In the case of the proposed SAV-based criteria, divergence from the idea that the only relevant parameters to measure are those related to drinking, swimming, and fishing is necessary. I think the fact that government management was involved in the topics covered by these papers indicates that such a change in attitude is beginning to occur: risks to the health of the natural, non-human populations in an environment are being taken into consideration as well as those to the people who use the resources.

Natural Variability

The final theme emerging from this meeting was the need to know the scales of natural biological variability in marine ecosystems and the need to integrate this information with that on changes in systems that have occurred as a result of anthropogenic forcing. This idea was not the target of a specific session but it surfaced in a number of talks, nevertheless. An example of the importance of this topic in a study was provided by the plenary session with Prof. Piet Nienhuis. In addition to the anthropogenic changes in the Oosterschelde that were monitored during the mid-1980s, the estuary also experienced several unusually severe winters during the time when the tidal barrier was being constructed. Professor Nienhuis emphasized that responses of the estuarine communities to the construction of the barrier could not be accurately assessed since the natural stress put on this system by the severe winters of 1985-86, 1986-87, and 1987-88 may also have caused changes in the floral

and faunal communities. The magnitude and long-term variability of natural stresses must be taken into consideration with any examination of man-induced changes in ecosystems. Although the idea of the importance of integrating natural variability with anthropogenic changes was not thoroughly explored at this meeting, I believe it is an important topic and will become the focus of much scientific research in the near future.

CONCLUSIONS

The significance to the marine science community of this joint ERF-ECSA meeting may well lie in the decisions made by the boards of the two organizations at this meeting. The boards met jointly for the first time and passed several resolutions. They resolved to continue the interactions between the two organizations by establishing regular correspondence between the board members and by planning another joint meeting in 1996. In the meantime, they will initiate efforts to actively assist estuarine scientists in eastern Europe, South America, Africa, and Asia through journal subscriptions and travel subsidies. They also plan to actively lobby Congress, Parliament, and other legislative bodies for the study and protection of estuaries in all countries. Eventually, these efforts may result in the formation of one international estuarine society by the end of the century.

The Estuarine Research Federation meetings have traditionally been one of the few fora in the U.S. where academic scientists doing basic research, government scientists doing applied research, and government people responsible for management and policy decisions, all on marine environmental issues, come together for discussions. Most scientific meetings tend to draw the first two groups, and government-sponsored meetings tend to attract the second two groups. The attendance of all three groups at these meetings has in the past promoted discussions of how the results of scientific research can be integrated with policy decisions to develop sound management of marine resources. This integration is critical if we are to protect and maintain natural marine ecosystems for the future.

This issue of scientific input to policy decisions is particularly relevant to the Navy since it operates in the marine environment and yet is expected to have minimal impacts on that environment. The Navy, on its own, funds significant amounts of basic research on marine processes, but much of this research is not directed toward those natural systems where the Navy may have a major environmental impact and where it is likely to focus future operations: estuaries, bays, and near-coastal environments.

Recently, the Office of Naval Research has developed a new research initiative that is specifically designed to address some of these concerns. This program will fund research across many scientific disciplines and has two major thrusts:

- Research on the processes controlling the fate and effects of toxic substances in estuarine and near-coastal marine environments; and
- Research in the science required to develop materials and procedures for use in environmentally sound ships.

It is hoped that the results in the first area will provide significant insight to the mechanisms that control the distribution, speciation, kinetics, and biological availability of toxicants that have come into the marine environment. Results in the second area should elucidate chemical, physical, and biological processes that can ultimately be applied to the development of environmentally compatible materials and operating procedures required to run a warship in such a way that its discharges have a minimal impact on the marine environment.

Oceanography

Who's Doing What in U.K. Ocean Engineering—The Marine Technology Directorate

by CDR John A. Sampson, USN, Undersea Systems Liaison Officer, Office of Naval Research European Office.

KEYWORDS: oil and gas exploration; subsea vehicles; ocean environment; non-hydrocarbon resources

INTRODUCTION

The Marine Technology Directorate Limited (MTD) is a focused research funding agency serving the offshore and maritime industries. Privatized by the government of the United Kingdom (U.K.) in December 1986, it manages projects for both the government's Science and Engineering Research Council (SERC) and about 50 member companies. Total funding last year (1991/1992) was £3.91 million (approx. U.S. $6.2 million), of which SERC provided £2.49 M and the Ministry of Defence (MOD) provided £291,000. The MTD divides its programs into two basic groups: those that receive SERC funding and those that do not.

SERC-FUNDED PROGRAMS

The five major areas receiving SERC funding are:

- Oil and Gas Exploration and Production
- Offshore Oil and Gas Structures
- Subsea Vehicles and Tasks
- Ships and Transportation
- Ocean Environment and Non-hydrocarbon Resources

These group descriptions are different from those used in previous years. Results from the managed research programs are normally held in confidence by the sponsors for a limited period, usually six months. Despite the obvious emphasis on North Sea oil and gas production, a significant amount of the research funded by MTD is in areas of interest to the U.S. Navy research and development (R&D) community.

Oil and Gas Exploration and Production - £622,063 (1991/1992)

The two principal programs in this area are primarily concerned with the topside processing of the oil, gas, water, sand, added chemicals, etc., that come up the well:

- Design and instrumentation of primary separation systems (£98,806), and
- Treatment of water offshore (£266,130).

Other individual projects include: pattern classification techniques for seismic event tracking, clay/polymer interactions, ultra-low tension risers, bubble dynamics in inclined pipes, and several others (total £257,127).

Offshore Oil and Gas Structures - £1,252,895 (1991/1992)

Six directed programs and 17 individual projects fall in this area. The six programs are:

- Defect Assessment in Offshore Structures (£38,667)
- Corrosion Fatigue Fracture Mechanics (£193,211)

- Behavior of Fixed and Compliant Offshore Structures (£423,511)
- Cost Effective Use of Fibre Reinforced Composites Offshore (£182,805)
- Influence of Welding on the Performance of High Strength Steels Offshore (£123,895)
- Decommissioning and Removal of Offshore Structures (£46,479).

The individual projects concern topics such as numerical techniques, physical testing, response of structures to explosions (e.g., during decommissioning), the behavior of piles, and the properties of concrete under very high hydrostatic loading (total £326,227).

Subsea Vehicles and Tasks - £1,076,098 (1991/1992)

The two directed programs and nearly all the 24 individual projects in this area concern unmanned underwater vehicles. The two programs, both of which were completed in 1992, were:

- Automation of Subsea Tasks (£283,814)
- Enhancement Technology for Underwater Vehicles (£220,557).

The principal areas covered included: sonar interpretation, vision systems, sensor integration, manipulator coordination, stability and control, navigation and positioning, and acoustic communications.

A new two-year, £1.5 million program [Technology for Unmanned Underwater Vehicles (TUUV)] was started in October 1992 to continue and expand the successes of the previous programs. [See "Technology for Unmanned Underwater Vehicles," *ESNIB*, this issue.]

The individual projects included research into subsea life support, remotely operated vehicle (ROV) control and guidance, low-drag vehicles, acoustic communications and signal processing, control of manipulators for nondestructive testing/inspection, acoustic holography, automated interpretation of inspection data, electrochemical cutting, and plasma welding (total £571,727; £138,944 from the MOD).

Ships and Transportation - £777,741 (1991/1992)

The single directed program in this area started in early 1992:

- Maneuverability of Ships: Estimation Schemes (MOSES) (£35,868)

The goal of this program is to improve the understanding of the complex hydrodynamic flows past a maneuvering ship, particularly vortex-shedding and the interactions of hull, rudder, and propeller.

Individual projects cover a broad range of topics, including: advanced numerical models, control and maneuvering, electric propulsion, machinery noise propagation, fabrication techniques, ship-model hydrodynamic testing techniques, electronic charts, stability prediction, shipboard fire modelling, fibre-reinforced plastic control surfaces, and a nonexplosive line-throwing device (total £741,873; £151,851 from the MOD).

Ocean Environment and Non-hydrocarbon Resources - £180,733 (1991/1992)

Most U.K. government funding in this area is not channeled through MTD. Nonetheless, MTD has decided to establish a foothold and is supporting 12 individual projects: three on engineering aspects of marine aquaculture, two on hard mineral extraction, one on shoreline wave energy, one on marine pollution from a subsea hydrocarbon release, and the remainder on basic oceanography and seabed geotechnics.

MULTI-SPONSOR PROJECTS

In addition to the above partially SERC-funded programs, MTD initiates and manages its own portfolio of Multi-Sponsor Projects (MSPs). These projects are generally too commercially oriented to receive SERC funding. Not surprisingly, oil companies are the major supporters of the MSPs, some of which include:

- *Dynamics of Fixed Marine Structures* (known in the industry as "UR8"), a guidebook on the dynamic design of fixed offshore structures subject to wave and current loading; currently in its third edition.

- *An Appraisal of Marine Growth on Offshore Structures*, first edition published in late 1992 to simplify and standardize marine fouling assessments within the industry.
- *Development of a Method for Acceptance Testing of Underwater Video*. This project, funded by AMOCO, ARCO, British Gas, British Petroleum, Chevron, Elf, Marathon, Philips, Shell, and Texaco produced the first industry standards for underwater video testing procedures and acceptance criteria. A rugged portable test kit has also been produced.
- *Major New Review of Offshore Structures and Pipeline Repairs*, has been surveying all significant repairs since 1981, including sections on causes of defects/damage, detection of defects/damage, nature of defects /damage, effects of defects/damage, repair options, repair methods chosen, implementation of repairs, and effectiveness of repairs. (Publication date not given, but probably within the next year or so.)
- *A Guide for the Engineering Analysis of Floating Structures*, planned to be similar to highly regarded guide for fixed structures noted above. The U.K. Health and Safety Executive and the Norwegian Petroleum Directorate are major supporters of this project. (Publication date not given.)

Additional proposals under development include:

- Quantitative Risk Assessment
- Pipelines (potential for 6 projects)
- Noise and Vibration Control for Offshore Structures
- Noise-induced Hearing Loss in Divers
- Flexible Risers and Umbilicals
- Definition of Research Requirements for Tourist Submarines
- Impact Analysis for Offshore Structures.

COOPERATIVE ARRANGEMENTS

The Marine Technology Directorate is a member of the following British organizations:

- Society for Underwater Technology (SUT)
- British Maritime Technology, Ltd. (BMT)
- Confederation of British Industry
- Institute of Marine Engineers
- Engineering Council
- Industrial Society
- Parliamentary Maritime Group.

The MTD participates in the following international programs:

- European Community Marine Science and Technology (MAST) Program
- European Community Maritime Industries Forum
- West European Graduate Education in Marine Technology (WEGEMET)
- University Enterprise Training Partnership in Marine Science and Technology (UETP-MST)

The MTD has also established bilateral collaborative agreements with:

- The French National Institute for Exploitation of the Seas (IFREMER) to explore various areas of subsea technology, including underwater communications, subsea lasers, underwater power sources, materials for deep submergence vehicles, and subsea installation protection.
- The Netherlands Foundation for the Coordination of Maritime Research (CMO) to study human factors in ship bridge operations.

SUMMARY

The MTD is probably the best single point of contact for learning who's doing what in ocean engineering in the U.K. The managers are quite helpful, within the constraints of commercial confidentiality, in providing information on their programs and members.

Point of Contact

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Technology for Unmanned Underwater Vehicles

by CDR John A. Sampson, USN, Undersea Systems Liaison Officer, Office of Naval Research European Office.

KEYWORDS: unmanned underwater vehicles; sidescan sonar; sensory deprivation; acoustic image; neural net

INTRODUCTION

Technology for Unmanned Underwater Vehicles (TUUV) is a major new United Kingdom (U.K.) research program. It is managed by Marine Technology Directorate, Ltd., for the government's Science and Engineering Research Council (SERC), the U.K. Ministry of Defence (MOD), and a consortium of member companies (typically offshore oil and gas companies). This two-year, £1.5 M (approximately U.S. $2.3 M) program began in October 1992 and builds on two previous programs: Automation of Subsea Tasks, Phases I-III (1985-1992) and Enhancement Technologies for Underwater Vehicles (1990-1992). SERC has committed £1.0 M to TUUV, with the remainder coming from member companies.

TUUV is specifically aimed at improving unmanned underwater vehicles for six major missions in the North Sea oil and gas fields:

1. Pipeline Surveys, including inspection and routing
2. Offshore Platform IRM (Inspection, Repair, Maintenance)
3. Wellhead and Satellite Wellhead IRM
4. Seabed Object Detection and Classification
5. Subsea Construction
6. Wet Salvage

The similarity to naval missions is obvious.

RESEARCH PROJECTS

Twelve individual research projects were selected for TUUV funding. All except TU4 have started work as of 9 April 1993.

TU1: Techniques for the Processing of Sidescan Sonar from Large Data Sets
(Herriot-Watt University, £119K)
Investigators: Dr. L.M. Linnett, Dr. K.E. Brown

Objectives:
- Develop algorithms and techniques to automatically process entire sidescan seabed surveys, especially for pipeline route surveys, pipeline inspection surveys, and seabed mapping
- Establish a standard database of seabed textures from sidescan sonar surveys

Comment: The approach seems to be to use fractal techniques to characterize seabed sediment textures and then to use statistics to identify abnormalities (e.g., objects, geological differences) in the texture. The actual object detection algorithm is adjusted based on the local seabed texture. The U.K. Defence Research Agency (DRA) and British Petroleum (BP) have provided extensive high-resolution sidescan sonar data to the investigators.

TU2: Probabilistic Sensor Fusion for Reliable Workspace Sensing
(Herriot-Watt University, £126K)
Investigators: Prof. G.T. Russell, Dr. M.J. Chantler, Dr. R.M. Dunbar

Objectives:
- Conduct a qualitative and quantitative assessment of the accuracy and reliability of a probabilistic sensor system for underwater robots
- Further develop probabilistic fusion algorithms and sensor models
- Compare optical and acoustic sensors.

Comment: The main problem being addressed is the "sensory deprivation" experienced by ROV manipulator arm operators who currently must view their work via a series of disjointed, individual video and sonar displays. This project seeks to fuse the information from a variety of sensors to continuously obtain and update an accurate representation of the ROV's immediate environment for, say, a 10-meter radius. The word "probabilistic" refers to their use of rigorously calibrated error models for each of the sensors to determine and explicitly represent the confidence in the accuracy of the fused sensor data. The sensors included in this project include a high-resolution sonar, a laser triangulation device, and video cameras. Although not an explicit part of this project, sensor fusion of the sort under investigation here is a crucial building block for not only creating a "virtual reality" work environment for a human operator but also for totally automating these tasks.

This project directly supports Herriot-Watt's manipulator project, TU5.

TU3: A New Underwater Vision System
(Strathclyde University, £125K)
Investigators: Prof. Gordon Hayward, Mr. R. Chapman

Objectives:
- Design and evaluate a 2-D matrix ultrasonic array for generation of 3-D images
- Merge the acoustic data with 3-D optical data, obtained from a stereo pair
- Create improved, robust stereo matching algorithms by fusion of the acoustic and optical data
- Construct and evaluate a prototype 3-D acoustic/optic underwater vision system.

Comment: This project seeks to fuse the 3-D image produced by a high-performance planar ultrasonic transducer array with the 3-D image produced by a pair of video cameras viewing the same scene. The thought is that the acoustic image, although coarser than its optical counterpart, will provide range and surface orientation information, which can be difficult to derive from passive optics, particularly for smooth surfaces. [N.B.: Professor Hayward has an excellent international reputation in the field of ultrasonic transducers and has an ongoing relationship with the Office of Naval Research (ONR) and U.S. Navy laboratories.]

TU4: Neural Network Architecture for Self-tuning, Adaptive Control of UUVs
(Liverpool University, £84K)
Investigators: Prof. J. Lucas, Dr. M.T.C. Fang

Objectives:
- Develop a neural net controller for a UUV
- Provide the controller with real-time, self-learning capability
- Test the performance of the controller in water.

Comment: The UUV functions to be tackled by this project include maintaining a steady position while performing a given task and following a prescribed trajectory to a worksite. The controller is to be self-learning, such that it continually learns and optimizes its control while on the job. An advantage to this sort of control is its ability to handle unanticipated situations. This project is currently "on hold".

TU5: Advanced Control of Manipulators
(Herriot-Watt University, £224K)
Investigators: Dr. D.M. Lane, Mr. M.W. Dunnigan

Objectives:
- Design, implement, and test manipulator task planning
- Further design, implement, and test the module that provides joint space input for hybrid position/force control, including obstacle avoidance
- Investigate and implement adaptive force control
- Attempt genuine coordination between two arms.

Comment: The goal of this project is to develop a two-arm manipulator system capable of performing typical offshore tasks with only supervisory control by the operator. That is, the operator will only need to specify tasks to be performed rather than directly control the arms in the usual

master-slave fashion. Development of a robust supervisory manipulator control system will significantly reduce both operator fatigue as well as dependence on high bandwidth communications. Thus, manipulator control via an acoustic datalink could become a realistic option. The ability to coordinate the use of two manipulator arms in the same workspace, and their dynamic interactions with the vehicle, will greatly improve the utility of IRM UUVs.

This project is being done in conjunction with TU2.

TU6: High Data Rate Subsea Communications for UUVs
(Newcastle University, £191K)
Investigators: Dr. O.R. Hinton, Mr. A.E. Adams, Dr. B.S. Sharif

Objectives:
- Determine the fundamental limitations relating to the use of *m*-ary PSK, beamforming, and adaptive equalization in the subsea environment
- Develop a half-duplex link using simultaneous beamforming at the transmitter and the receiver
- Demonstrate the practicality of a high-data-rate acoustic communications system operating in real conditions (e.g., ≈ 20 kbps at ≈ 3 km horizontal range in shallow water).

Comment: The fundamental issues to be investigated are:

1. The phase coherence of the acoustic signals that is affected by small-scale inhomogeneities such as turbulence and thermal gradients, especially those created by the movement of the vehicle,
2. adaptive beamformer and equalizer performance, and
3. Receiver/demodulator performance, especially the ability to correctly detect bits in the presence of phase jitter and multipath.

This project seems very similar to some of Josko Catapovic's work at Woods Hole Oceanographic Institute.

TU7: A Self-Contained Navigation System for UUVs Operating Around Subsea Installations
(Strathclyde University, £136)
Investigator: Prof. Chengi Kuo

Objectives:
- Perform a series of laboratory experiments to generate a database of sonar signals for various structural arrangements
- Repeat some experiments offshore to validate laboratory results
- Integrate the sonar data with engineering drawings of the structure to provide navigational information.

Comment: The goal of this project is to establish the principles for an acoustic UUV navigation system that does not require the placement of acoustic transponders, only the engineering drawings of the structures in the area. The emphasis of this project is on in-water acoustic experimentation, contrasted with the outwardly similar TU9 at Liverpool, which is primarily concerned with optical sensing and computer modelling.

TU8: A Study of Multi-Spectrum Data Association for the Precision Navigation of UUVs
(Glasgow University, £71K)
Investigator: Dr. C. Goodchild

Objectives:
- Demonstrate the feasibility of using the global positioning system (GPS) for UUV 3-D navigation
- Establish a general specification for the macro navigation multi-spectrum data association process
- Produce a specification for a UUV macro navigation technology demonstrator.

Comment: The concept is to deploy a pattern of least four floating buoys (or three plus the surface support ship) containing differential GPS receivers that transmit their positions and GPS time to the UUV via an acoustic data link. The UUV will compute its 3-D position based on the times of

arrival of the signals from the buoys. An inertial navigator in the UUV will aid in resolution of multipath by maintaining an expected time-of-arrival window for the next signal from each buoy.

TU9: Navigation of a UUV Within Structures Using Fusion of Sensor Data and World Modelling Techniques
(Liverpool University, £92K)
Investigators: Prof. J. Lucas, Dr. J.S. Smith

Objectives:

- Use position, orientation, and range images (either optical or acoustic) together with a world model to find the absolute position of a UUV within a structure
- Produce upgrades to the world model during the life cycle of the investigation.

Comment: The concept is to first create a computer "world model" of the structure, using the IGRIP software package from Deneb Robotics Inc. An image is then generated based on the field of view of the selected sensor at the UUV's estimated position. The difference between that image and the real image from the sensor is used to determine the UUV's position, probably by an iterative process. This technique should be applicable to both optical and acoustic sensors. However, this project will use only optics. This project emphasizes computer modeling and optical imagery, contrasted with the outwardly similar TU7 at Strathclyde, which is primarily concerned with in-water acoustic experimentation.

TU10: Design Studies of Power Electronic Drives Systems for Thrusters of UUVs
(Southampton University, £55K)
Investigator: Prof. M.R. Harris

Objectives:

- Appraise the technical requirements, objectives, and trade-offs of the thruster drive system specifically for vehicles conducting offshore platform IRM
- Identify alternative system strategies, covering both tethered and untethered vehicles
- Conduct in-depth design studies of promising strategies.

TU11: Snap Loading of Cables During Launch and Recovery of Tethered Subsea Units
(Strathclyde University, £53K)
Investigator: Dr. Dracos Vassalos

Objectives:

- Understand the nature of cable slack and snap loading of marine cables
- Establish suitable equations governing cable dynamics
- Validate the proposed theory against available experimental results
- Conduct a parametric investigation to identify and quantify the key influencing factors.

Comment: The first phase of the project is to conduct a theoretical analysis of the mechanisms causing slack and the nature of the ensuing snap loading. It is expected that three cable-tension regimes, governed by different equations, will be important:

1. Positive high tension — this has been extensively studied and the governing equations are thought to be well understood
2. Low tension — this has not been studied as much, and the usual assumptions (e.g., that bending stiffness is not important) may not be valid.
3. Zero or slight negative tension — very little research seems to have been done for this condition; a suitable equation needs to be developed.

Dr. Vassalos plans to combine the equations governing these three regimes into a single, unifying equation. The next phase will be a numerical validation of this equation by using published experimental data. The validated equation will then be used to evaluate the effects of various parameters such as cable elasticity, length, buoyancy of the attached UUV, frequency and magnitude of excitation, and launch speed on the occurrence of cable slack.

TU12: ***Hydrodynamics of UUVs Near the Air/Sea Interface***
(Strathclyde University, £99K)
Investigators: Dr. P.G. Sayer, Dr. A.H. Day

Objectives:
- Determine experimentally the added mass and damping coefficients of representative UUVs in the wave-affected near-surface zone by using forced oscillation tests in calm water
- Measure the loads exerted by steep waves on UUVs held fixed near the air/sea interface
- Use 3-D diffraction theory to compute these coefficients and loads
- Assess the level of correlation and the scope for interpolation and extrapolation among the results obtained by these three approaches.

Comment: This is primarily an experimental project using Strathclyde's large seakeeping test tank.

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Coastal and Nearshore Research at the Laboratori d'Enginyeria Maritima (Polytechnical University of Barcelona, Spain)

by Steve Elgar, School of Electrical Engineering and Computer Science, Washington State University, Pullman, Washington.

KEYWORDS: oceanography; coastal morphology; marine climate; sediment transport; numerical models

INTRODUCTION

The Laboratori d'Enginyeria Maritima (LIM/UPC) is a research center associated with the Department of Hydraulic, Maritime, and Environmental Engineering of the Universitat Politecnica de Catalunya (Polytechnical University of Cata-lunya), located in Barcelona on the Mediterranean coast of northern Spain. Barcelona is a modern, cosmopolitan city with a thriving international community, and thus attracts students and researchers from many countries.

Officially, the laboratory is termed a nonprofit, public research center, but the relationship of the laboratory to the university is similar to that of research laboratories located at universities in the United States. The members of the laboratory teach engineering and oceanography undergraduate and graduate students as well as perform research and consulting. Funding comes partially from the national and local governments, the European Community, and private industry. About three-quarters of the annual budget is associated with research projects. Between 1987 and 1991 research contracts with companies, public administration departments, and other research centers totaled about $6 million (U.S.). About 30 professionals are employed full-time by the laboratory, along with a varying number of visiting scientists and engineers. Most of these 30 people are

researchers, with 10 having additional responsibilities for teaching in the university and 4 having managerial responsibilities.

The main aims of the laboratory are basic research, applied research and technological development, and diffusion and transfer of knowledge. A board of directors was established in 1990 to direct the laboratory toward reaching its goals and to ensure a wide participation in the laboratory's work. The board members represent the university in Barcelona, the local government, the department of public works in Barcelona, the Spanish national Center of Studies and Experimentation in Public Works, the ports of Barcelona and Bilbao, and the University of Cantabria. The laboratory's projects are further divided into 6 (at present) areas:

- Marine Climate
- Coastal Hydrodynamics
- Oceanographic Engineering
- Coastal Morphology
- Marine and Estuarine Pollution
- Harbor and Coastal Engineering.

In addition to teaching, both basic and applied research are conducted within each area. The results from basic research are published in refereed journals such as the *Journal of Geophysical Research; Coastal Engineering; ASCE Journal of Waterways, Port, Harbor, and Coastal Engineering*; and the *Journal of Coastal Research*. In addition, members of the laboratory attend and host international conferences and publish in the associated proceedings. Although almost all members are Spanish nationals, most speak and write English fluently (as well as other languages). The applied research is in part directed toward solving problems in the coastal environment of Spain (both Mediterranean and Atlantic Oceans). The undergraduate students obtain degrees in ocean or civil engineering that are equivalent to a masters degree in the U.S. Doctoral students are expected to perform research and publish original contributions in the open literature, similar to their American counterparts. Upon graduating, the Ph.D.'s obtain employment in university and government research as well as in industry either in Spain or in their home countries (there is a mix of Spanish and international graduate students).

BASIC RESEARCH

The LIM carries out basic research in three main areas. Marine hydrodynamics research involves formulating the equations of motion for hydrodynamic processes in the nearshore/coastal region and developing numerical models based on the equations. Limited field experiments have been conducted to verify the models. This research has also been extended to deeper water, and models for the Catalan-Balearic Sea (western Mediterranean basin) and the Bransfield Strait (Antarctic Ocean) have been developed. Marine climate research has focused on numerical studies of the transformation and evolution of the directional spectrum of wind-generated waves. Sediment transport and coastal evolution mechanisms are also being studied, primarily in association with a large project to study the stabilization of the Ebro Delta south of Barcelona on the Mediterranean coast. The main goal is to analyze and evaluate sediment transport resulting from waves and currents.

APPLIED RESEARCH AND TECHNOLOGICAL DEVELOPMENT

Applied research is performed in the same areas as basic research. Harbor authorities, private companies, and government institutions commission studies of particular coastal sites, and LIM provides numerical models of wave propagation, currents, and tides. The marine climate research is applied to developing a database of wave, current, and wind conditions to allow engineers to design coastal structures appropriately. Software is being developed to forecast the impact on coastal morphology of changes in the nearby coastal environment, both man-caused (e.g., construction of harbors) and natural (e.g., sea-level rise).

DIFFUSION AND TRANSFER OF KNOWLEDGE

The staff of LIM teaches university courses in maritime engineering to both civil engineering and technical public works students. A new course of study in ocean sciences to be jointly taught by the Polytechnic and the University of Barcelona is being developed. In addition to undergraduate

engineering and science programs, LIM has an active graduate program.

LIM organizes regular training courses for professionals such as engineers working in private industry, port and harbor managers, and scientists. In addition, LIM has hosted several international conferences, including the Third International Conference on Numerical Grid Generation (1990) and the Second International Conference on Computer Modelling in Ocean Engineering (1991). An international conference on large laboratory and field programs to study the nearshore region is scheduled for 1994.

SPECIALTY AREAS

Marine Climate

Research topics in the marine climate specialty area are related to analyzing and forecasting the propagation of wind waves and associated currents. Recent work involves studies of average and extreme conditions for wind waves and currents, spectral analysis of wave measurements, wave forecasting from wind data, numerical simulation of waves and currents, models of wave refraction and diffraction, and modelling of the penetration of waves into harbors.

Coastal Hydrodynamics

LIM has recently been studying the hydrodynamics of the nearshore region, in particular, waves and currents in the breaking zone. Studies of breaking-induced turbulence have led to the development of the HYDROTUR numerical model. Recent research has been directed toward modeling the transformation of waves from deeper water depths to the breaking region, especially the associated currents in the nearshore region. The staff at LIM is developing three-dimensional nearshore circulation models that predict nearshore circulation. Some of this research is funded by the European Community (EC) Marine Science and Technology (MAST) program.

Oceanographic Engineering

This new interdisciplinary area of interest at LIM includes studies of the large-scale hydrodynamic processes that govern the behavior of biological and sedimentary systems on continental shelves. To accomplish the goals of this area, hydrographic surveys are performed and meteorological variables are monitored. A system of autonomous instruments (wave buoys, tide gages, current meters, satellite images, etc.) is being deployed. Numerical models of circulation in open-ocean conditions are also being developed.

Coastal Morphology

The main aims of this research area are to identify, quantify, and eventually predict the morphological processes that take place along the coast. Field studies are being made to measure coastal bathymetry and sediments. They include groundbased and aerial surveys, sediment sampling and budget analysis, and numerical modeling.

Marine and Estuarine Pollution

This is the newest research area established at LIM and includes field measurement programs, laboratory studies, and numerical simulations to investigate pollution in the coastal zone.

Harbor and Coastal Engineering

The many harbors in Spain are vital to both shipping and tourism. The LIM provides design, planning, and optimization of inner and outer harbor structures, as well as design of coastal protection works. In addition, the LIM studies the impact of these works on the adjacent coast.

INFRASTRUCTURE

Accomplishing the goals of the LIM requires laboratory experiments, field studies, and numerical models. The laboratory has recently installed a very long wave flume (100 m long by 3 m wide by 5 m deep) in a new laboratory building. This flume has a wedge-type wave paddle that can generate 1.6-m high waves. The laboratory also has the capability to simulate nearshore conditions for studies of circulation, wave breaking, and the effects of coastal works. A wave basin capable of generating directionally spread wave fields is being designed.

The field measurements program currently consists primarily of standard wave and wind measuring devices, such as buoys, tide gages, and current meters. Programs to measure waves and currents in the nearshore are just beginning. Sediment transport along the coast is measured with standard survey equipment and with aerial photography.

The numerical models are run on local workstations and on a Cray-XMP and an IBM 3090 located at the Barcelona Supercomputer Center. The laboratory has INTERNET connections to allow international access to other workstations and electronic mail.

SUMMARY

The Laboratori d'Enginyeria Maritima (LIM) is a research center associated with the Department of Hydraulic, Maritime, and Environmental Engineering of the Polytechnical University of Barcelona, Spain. It has 30 permanent scientists and engineers investigating a range of topics of importance to coastal and nearshore oceanography, including waves, currents, winds, tides, circulation, and sediment transport. LIM performs basic and applied research and teaches both undergraduate and graduate students. Current basic research emphasizes the development of numerical models to predict coastal and nearshore wave propagation and circulation. The applied research is aimed toward solving site-specific problems along the Spanish coast. The investigators at LIM collaborate with researchers both within and outside of Spain, especially in basic research and guidance of graduate students.

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THE EMBASSIES: TECHNOLOGY ROUNDUP

FEDERAL REPUBLIC OF GERMANY

German Research and Technology Budget—Big Science, Big Money, Big Controversy

For further information on Federal Republic of Germany items, contact Mr. Jim McCracken, Science Counselor, American Embassy, Bonn, FRG, Box 280, APO NY 09080-7400.

The 1993 draft budget for the Ministry of Research and Technology (BMFT) (Table 1), the primary funding source for German nonacademic research, earmarks DM 9.603 billion* for the agency, a 3.8 percent increase over last year's target budget of DM 9.254 billion. Furthermore, the BMFT is no longer responsible for promoting industrial-use agricultural products such as alternative fuel sources, which now fall under the jurisdiction of the Ministry for Food, Agriculture and Forests. This change will result in a 9.8 percent drop from 1992 levels in BMFT funding of research regarding renewable energy sources and rational energy use.

Additional funding of DM 272 million for 1993 will be available through the Ministry of Finance for continuing BMFT'S participation in university innovation programs for the new states (länder). Of the additional funding, DM 222 million is earmarked for continuing the scientist-integration program, which provides transitional funding for former German Democratic Republic (GDR) scientists transferring from the former Academy of Sciences to universities in the Eastern portion of the Federal Republic of Germany (FRG), and DM 50 million for a new investment program to benefit

*Exchange rate used: DM 1.49 = U.S. $1.00.

Table 1 — Draft Budget for the Ministry of Research and Technology (BMFT)

Field	Amount (DM million)	Percent of Total	1993/92 Increase (percent)
Total BMFT Budget	9,602.7	100.0	3.8
Overall Basic Research Budget	1,674.0	17.4	7.5
Basic Financing for Max Planck Society	622.8	6.5	12.2
Large-scale, basic research instrumentation	1,051.2	10.9	4.9
Long-term state programs	2,351.2	24.5	3.9
Ocean research	129.9	1.4	0.6
Polar research	70.6	0.7	−3.6
Space research & technology	1,815.9	18.9	4.5
Nuclear fusion research	206.1	2.1	0.3
Geological science (incl. deep drilling)	129.0	1.3	8.9
Environmen . health research and other	1,729.1	18.0	6.7
Ecological research	288.3	3.0	7.6
Environmental technology	260.0	2.7	−3.2
Climate & atmospheric research	165.1	1.7	8.2
Health/medical R&D	512.0	5.3	7.2
Work & technology	83.5	0.9	−5.8
Historic monument preservation	35.0	0.4	−15.5
Arts & humanities; social sciences	138.1	1.4	7.3
Miscellaneous activities (incl. DM 30 million for CIS)	247.1	2.6	26.4
Promotion of technology and innovation	3,939.7	41.0	0.8
Basic financing Fraunhofer Society	364.3	3.8	9.9
Ocean technology	47.8	0.5	−21.3
Coal and other fossil fuels	107.8	1.1	−17.4
Renewable energy sources & rational energy use	348.1	3.6	−9.8
Nuclear energy research	325.3	3.4	−4.7
Residual costs of nuclear research establishments	268.5	2.8	18.9
Information science (including production technology)	1,014.9	10.6	1.9
Biotechnology	296.9	3.1	−2.1
Materials research	258.3	2.7	3.5
Technology of the 21st century	256.3	2.7	6.4
Aviation research & hypersonic technology	203.1	2.1	−3.9
Research & technology for ground-based transportation & traffic	169.1	1.8	0.1
Raw material safeguarding	0.9	0.0	−64.0
Infrastructure innovation & improvement	187.0	1.9	14.0
Special publications & information	91.4	1.0	−5.1
Budget cuts not yet specified	−180.0	−1.9	0.0
Federal Ministry	88.4	0.9	5.2
University innovati..n program (from Finance Ministry)	272.0		20.4

*Note: Exchange rate used: DM 1.49 = U.S. $1.00.

new state research facilities not associated with universities. Thus, the total funding available for BMFT programs in 1993 will be almost DM 9.9 billion.

In addition to the funds targeted for research establishments independent of universities, the budget emphasizes the strengthening of research and development (R&D) capabilities in small- and medium-size enterprises. Federal Research and Technology Minister Heinz Riesenhuber has outlined the following areas of emphasis in the 1993 budget:

- rebuilding the research capability in the länder, for which DM 1.75 billion has been slated, an increase of 9.4 percent over the 1992 budget of DM 1.6 billion.
- commitment to basic research, which will reach a new peak, accounting for just under 40 percent of the BMFT's total budget.
- increased funding for environment and health research, especially in the fields of ecological, atmospheric and climate research, as well as medical research. These fields of emphasis are intended to help the FRG meet the requirements of the resolutions set forth at the environmental summit in Rio de Janeiro. Total expenditures in these areas will constitute 18 percent of the BMFT's total budget, an increase from 9.2 percent in 1982.
- promoting strategic technologies for the twenty-first century, on which the global competitiveness of German industry will depend. The budget for this research will increase by 6.5 percent, to DM 256M.
- continuing the European cooperative work in space technology, with the goal of working to make the European Space Agency (ESA) adapt to and support the global political changes of the previous three years, particularly through establishment of cooperative ties with Eastern European Nations.

Fields of Emphasis

The following fields of research will receive high funding priority in the 1993 BMPT budget:

Strategic Technologies

The overall budget for promotion of technology and innovation is DM 3.94 billion, only a slight increase over the 1992 figure. In its promotion of strategic technologies for the twenty-first century, the BMFT will continue to emphasize information science, materials science, biotechnology, energy technology, and transportation technology. New areas of research include development of "functional" materials, thin-film technology, nano-technology for production of small structures, and bio-informatics.

Information Science

The BMFT'S information science funding of DM 1.01 billion will be complemented by as much as DM 470 million expected to be available through the European Community (EC) for research in this field. Areas of emphasis will include telecommunications, electronic components, applications of microelectronics, peripheral and systems technologies, as well as information processing. For telecommunications work, Deutsche Telecom is expected to provide an additional DM 900 million in funding, a large increase above the 1990 figure of DM 380 million.

Environment and Health Research

The BMFT'S funding of environment and health research, totaling DM 1.73 billion, will emphasize development of research capabilities in the länder. Health research will focus on cancer, AIDS, cardiovascular disease, mental illness, and rheumatism. One-third of the project funds in the area of environmental technology will be set aside for environmental restoration projects. In accordance with the decisions made at the environmental summit in Rio, the funds for atmospheric and climate research will be increased by 8.2 percent over the previous year, to DM 165 million. Since 1982, funding for environmental research has increased by more than 1000 percent.

Energy Research

Total funding of energy-related research will reach DM 1.26 billion in 1993. The BMFT will

be cutting back its funding of conventional electricity production research, claiming that previous research has been successful and that now the "market is ripe" for transfer of research breakthroughs. Funding for nuclear research will be concentrated in the areas of reactor safety and nuclear waste disposal, with a small amount for "inherently safe" reactor design. DM 258 million will be earmarked for closure and removal of nuclear facilities built in the 1960s and 1970s. Funding for decentralized photovoltaic generation will continue while funding for renewable energy and rational energy consumption will be scaled back within the BMFT, since the Ministry of Food, Agriculture and Forests will take over funding of research regarding agricultural products for industrial and energy use.

Space

The overall budget for space research and technology will be DM 1.82 billion, an increase of 4.5 percent over last year's budget. Funds for European space research will be increased by DM 70 million over the 1992 budget, to DM 1.23 billion. This increase will allow the FRG to continue its participation in the Columbus attached pressurized module (APM), the development of ARIANNE 5, and ESA's Earth observation and science programs, but Minister Riesenhuber has made it clear that there will not be sufficient funding to support HERMES or the man-tended free flyer (MTFF). While the new budget places greater emphasis on ESA programs, it provides DM 20 million for increased cooperation with the Commonwealth of Independent States (CIS) as well as funding for bilateral cooperative projects with the U.S., including the D-2 Space Lab Mission.

Geosciences

Overall funding for geoscience research will be DM 330 million. This field includes ocean research, polar research, and deep drilling projects. Overall geoscience funding in this fairly broad definition will increase by 4.9 percent over 1992 levels.

Cutbacks in the West—Growth in the East

The West

The 13 major federal research establishments in the "old states" will still receive the lion's share of BMFT funding for institutional research—DM 2.3 billion in the next year, about the same nominal level as in the previous two years. However, in real terms, the level of funding in nominal DM effectively results in funding cutbacks. For these research facilities in the "old states", the BMFT anticipates staff reductions of 1700 to 1900 employees by 1995, achieved primarily through mandatory retirement regulations for employees who are more than 58 years old.

In the past, large yearly increases in funding may well have given the scientific community expectations of continued growth, but the funding level of 1992 and 1993 has caused considerable controversy. This has added to the growing concern among (former West) German scientists that they may be enduring undue hardship in the federal government's massive efforts to revitalize the former Eastern portion of the FRG, where large BMFT funding increases will be directed.

Within the framework of level overall funding for western facilities, the BMFT has reprioritized research goals such that some facilities will be faced with nominal funding cuts, while others will continue to benefit from growing budgets. Reflecting the BMFT's de-emphasis of nuclear and related research, in the next three years, the following facilities will be particularly hard hit, facing major nominal funding cuts:

- The National Research Center in Geesthacht (GKSS), which until the late 1970s specialized in research on nuclear propulsion for ships; in the last 10 to 15 years emphasis has shifted to nuclear safety and environmental research and technology.
- The Society for Mathematics and Data Processing (GMD), specializing in information science and technology.

- The National Research Center in Juelich (KFA), which conducts nuclear and conventional energy research, along with research in a wide variety of other fields.
- The Nuclear Research Center in Karlsruhe (KFK), specializing in nuclear energy research and technology, also conducting research regarding the environment and microsystems technology.

In keeping with the BMFT's new emphasis on environment, health, and basic research, the following western facilities will receive significant funding increases in the next three years:

- The Alfred Wegener Institute for Polar and Ocean Research (AWI) in Bremerhaven, which will conduct research regarding global climate change.
- The German Electron Synchrotron (DESY) in Hamburg, where the major new proton-electron storage ring HERA has recently been placed into line.
- The German Cancer Research Center (DKFZ) in Heidelberg, which specializes in tumor virology research and formation of clinical cooperative groups.
- The Society for Heavy Ion Research (GSI) in Darmstadt, specializing in particle physics.

In 1993, BMFT funding for the Max Planck Society (MPG) will increase by 12.2 percent over the 1992 level, to DM 623 million, as part of the BMFT's increased support for basic research, which is the focus of the various MPG institutes.

Funding by BMFT for the Fraunhofer Society, which works to transfer scientific knowledge from academia to industry, will also increase in 1993, to DM 364 million up by 9.9 percent from the 1992 level.

The East

In the länder, three new national research establishments are being built:

- The Environmental Research Center in Leipzig-Halle, which will initially focus on characterizing environmental degradation in the former Eastern portion of the FRG.
- The Max-Delbrueck Center for Molecular Medicine in Berlin-Buch, a basic research facility that will develop integrated programs for disease diagnosis, therapy, and prevention.
- The Geo-Research Center (GFZ) in Potsdam will conduct research in all areas of geological science, including deep drilling projects and seismic research.

These new facilities, along with eight eastern branches of western national research facilities, will in total employ as many as 1700 people. In a joint funding agreement with state governments, the BMFT continues to provide 50 percent support to so-called Blue List facilities—24 research establishments and 4 branches of western research facilities, with a total of 3300 employees. The Fraunhofer Society has founded 9 institutes and 12 branches of western research facilities, with a total of 1050 employees, the Max-Planck Society 2 institutes, 28 working groups, and 7 centers, with a total of 900 employees. Research topics in these projects cover a wide spectrum, from natural sciences to arts and humanities.

Institutional promotion will be enhanced through the DM 272 million earmarked in the 1993 budget for BMFT support of the University Innovation Program (HEP) for the länder, a project managed by the BMFT. The 1993 budget also calls for implementation of a 4-year investment program for research establishments not associated with universities. The BMFT anticipates contributing approximately DM 50 million to this program, with state contributions bringing total investment to DM 400 million over the period from 1993 to 1996.

Promotion of research and technology (institutional promotion, project promotion for specific programs, and the BMFT portion of funding for the University Innovation Program) in the länder will in total constitute about DM 1.75 billion of the 1993 BMFT budget.

Overall, BMFT promotion of specific projects for 1993 will constitute approximately DM 4 billion of the total budget. Of this amount, DM 1.8 billion is slated for projects that will be conducted

in cooperation with industry. This emphasis on commercial viability addresses the concern within the scientific community that the FRG has not kept pace with Japan in converting research breakthroughs into economic gains.

With a planned funding level of DM 550 million, support of small and medium-sized enterprises constitutes about one-third of the total BMFt promotion of commercial projects. In comparison to their own expenditures for R&D, small and medium-sized enterprises now receive about three times as much support funding as large enterprises. Special emphasis within the small and medium-sized enterprise program is placed on supporting enterprises in the länder. These special programs will focus on:

- financially supporting increasing staffing levels to improve internal capacity for technical development within individual enterprises;
- financially supporting R&D work conducted by eastern and western research institutes for small and medium-sized firms who are currently unable to conduct such work themselves; and
- promoting the creation of technologically oriented enterprises.

The objective of this small and medium-sized enterprise promotion is to create an independent R&D infrastructure in the länder that can compete in both the German and European markets.

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